THE ELECTROLYTIC REDUCTION OF DEXTROSE TO SORBITOL IN ACID SOLUTION

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Erwin Maynard Koeritz

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To

my wife, without whose patience and understanding

this work would not have been possible

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TABLE OF CONTENTS

LIST OF FIGURES

THE ELECTROLYTIC REDUCTION OF DEXTROSE TO SORBITOL IN ACID SOLUTION

SUMMARY

Sorbitol is a hexahydric alcohol which has become an increasingly important industrial chemical in the last few years. It is employed in the synthesis of varnishes, resins, surface active agents and vitamin C and is rapidly entering the fields formerly served by other polyols. In the past, sorbitol has been produced commercially by the electrolytic reduction of dextrose, but the recent trend has been toward a process involving the catalytic hydrogenation of dextrose at high pressure.

There are undoubtedly many reasons why the electrolytic process has fallen into disuse. Among these are the relatively low reaction rates obtained, the difficulty experienced in controlling the product quality and the separation procedures required. The possibility of improving the commercial electrolytic process by careful control of operating variables in a modified process has been suggested by Emerson (15).

At high pH and elevated temperatures, dextrose is subject to extreme degradation. However, an alkaline catholyte is employed industrially because prohibitively low rates of reduction are obtained in acid solution, in which dextrose is much more stable. By proper control of the alkaline film which forms spontaneously on the cathode when electrolysis proceeds in an acid solution, it should be possible to obtain rates comparable to those realized when alkaline catholytes are

employed without the accompanying degradation. The use of a buffered acid catholyte, positive steps to insure formation of an alkaline cathodic film and the use of electroendosmosis of anolyte acid as a pH control mechanism are major characteristics of the modified process. This thesis is a report of the results obtained from the evaluation of these modifications and the study of the mechanisms of the process.

To facilitate an understanding of the results obtained during the experimental program, a discussion of the theory of electro-organic reduction, with particular attention to the reduction of dextrose, is included. The important factors such as electrode potential, depolarizing agents, and concentration of depolarizer are presented along with a consideration of the electrolytic reduction of dextrose in alkaline and acid media and the possible improvements in the process.

The apparatus includes, in addition to the usual arrangements for electrolysis work, an electronic power supply of novel design for automatically maintaining a constant flow of current despite wide variation in the resistance of the cell as the reaction proceeds.

The results include material balances on the operation, which are somewhat more complete than those reported in the literature. In contrast with previous investigations, the data include specific information on the determination of sorbitol as such, rather than an empirical index of sorbitol content. The extent of loss of carbon-containing compounds from the catholyte by diffusion through the permeable diaphragm is established.

Evaluation of the modified process in the light of the experi-

mental data indicates that while the fraction of dextrose converted to sorbitol is comparable to that prevailing in the commercial process, the rate of reaction of dextrose with hydrogen is somewhat lower. The alkaline cathode film is stable but quite thin due to the hindering effect which the catholyte buffer exerts on the formation of the film. The use of electroendosmosis as a pH control mechanism is not an attractive possibility.

Study of the mechanism of the process indicates a complex interrelation of the variables. However, the data permit several important conclusions. In considering the rate of reduction it is found that increase in cathode potential or pH is accompanied by increased reaction rates. In contrast to results obtained in unbuffered alkaline solutions, the rate of reduction is affected by the dextrose concentration.

The data are shown to be reliable, reproducible and compatible with existing data.

While the results obtained indicate the modified process, as proposed by Emerson, to be somewhat less effective than the existent commercial electrolytic process, the conclusions concerning the mechanism should be of considerable interest in other cases of electroorganic reduction under similar conditions.

INTRODUCTION

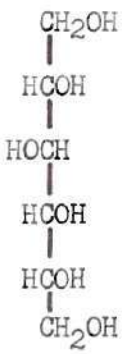
Industrial Importance of Sorbitol

In the last fifteen years, sorbitol has developed from a laboratory curiosity to an important industrial chemical. In 1951 over 22.5 million pounds were produced and with increased production facilities the output of sorbitol could well reach 75 million pounds in 1952 (1). With the exception of very few applications, such as anti-freeze and brake fluids, sorbitol has found a place in most cases where a polyhydric alcohol is used. Thus, sorbitol is a competitor to such polyols as glycerine, ethylene glycol, pentaerythritol, propylene glycol and di- and triethylene glycols.

The uses of sorbitol are many and varied. It finds application directly as a humectant and is used in the manufacture of synthetic resins, varnishes, surface active agents and vitamin C.

Before discussing the uses of sorbitol in detail, it is well to inspect the physical and chemical properties of this polyhydric alcohol.

Properties.--D-Sorbitol, a hexahydric alcohol, has the empirical formula $CH_2OH(CHOH)_4CH_2OH$. The structural formula may be written as follows:



Molecular Weight 182.1

Many of the characteristics of the other sugar alcohols or glykitols are found in sorbitol. These compounds are of general interest because of their solubility in water and hygroscopic properties. The organic monoesters of long chain fatty acids may possess surface active properties which make them of interest as emulsifiers or foam producing agents (2).

Pure D-Sorbitol is a white, odorless, crystalline solid at room temperature. Its density is 1.472 at -5°C. and the refractive index in 10 per cent aqueous solution is 1.3477 at 25°C.

Two crystalline forms are available, depending upon the method of crystallization employed. The stable form has a melting point of 97.7°C. and the metastable form melts at 93°C.

The heat of solution of sorbitol is -26.5 calories per gram. The heat of combustion has been reported to be 3994 calories per gram.

Sorbitol is very soluble in water, slightly soluble in methanol, ethanol, acetic acid, phenol and acetamide and almost insoluble in most other common organic solvents (3).

Sorbitol is widely distributed in nature. It is found in seaweed, tobacco and many fruits and berries. Strain (4) found the sorbitol content of thirty-four natural materials to range from zero to 10.4 per cent. None of the natural sources is of industrial importance.

Uses.--In 1950, about three million pounds of sorbitol were used for the production of vitamin C by fermentive oxidation.

In 1951, almost a billion pounds of the various polyols were used. Sorbitol is finding more and more application as a replacement for or

in conjunction with other polyols. It is enjoying increasing usage in alkyd resins and gums where it is usually used in equal weights with glycerol or pentaerythritol.

Because of the surface active properties of its esters, a large portion of sorbitol production finds its way into surface active agents such as the "Tween" or "Span" products made by the Atlas Powder Company.

Sorbitol is nitrated to yield the hexanitrate which is then used in high-explosive compositions. It is customary to nitrate glycerol-ethylene glycol solutions of sorbitol to yield low freezing, high-explosive liquids.

Sorbitol is widely used as a humectant or moisture conditioner in cosmetics, glues, paper, shoe dressings, textiles, food products, pharmaceuticals and tobacco. The tobacco industry alone uses almost 45 million pounds of polyols annually. Sorbitol is replacing glycerine for this use, not only because of its desirable hygroscopic properties and slightly lower price, but also because it improves the taste and odor of the smoke. It does not produce acrolein when it is burned. Its combustion products are related to those of sugars occurring naturally in the tobacco (3).

The surge in sorbitol consumption has been caused by several factors. The uses of sorbitol, both potential and actual, are large in number. While the cost of other polyols has risen, that of sorbitol has declined with increasing production. The raw materials necessary for its manufacture are relatively cheap and abundant, and the manufacturing process requires few critical materials, so that the sorbitol supply is quite reliable. This is of extreme importance to prospective

users.

Manufacturing processes.—Although references to sorbitol may be found widely scattered throughout the nineteenth century French and German technical literature, it appears that it was first isolated for study in 1872 by the French chemist Joseph Boussingault (3).

The chain of events which led to the present large scale production of sorbitol is rather interesting. During the first World War the Atlas Powder Company found that mannitol, the epimer of sorbitol, could be nitrated to produce a valuable explosive for use in blasting caps. Unfortunately, only limited quantities of mannitol were obtainable since the only source was the sap of the ash tree harvested in certain Mediterranean areas. There the natives collected the sap just as maple syrup is gathered in the United States. It was used as a mild laxative and an adjunct to diabetic diets. Such a source was not entirely satisfactory (5).

Following the war, Dr. H. Jermain Creighton of Swarthmore College developed a process for producing mannitol by the electrolytic reduction of dextrose in aqueous solution (6-13). Commercial production was initiated in 1937. The product of the electrolytic cell was found to contain appreciable quantities of materials other than mannitol. Among these side products, sorbitol occurred to the greatest extent. It soon became apparent that sorbitol, because of its extraordinary humectant properties, could command a good price. The complex product of the cell was consequently freed of mannitol and inorganic salts and sold as a concentrated, non-crystallizing syrup for conditioning purposes. During

the second World War the demand for sorbitol tripled, even though consumption was restricted to military and essential civilian requirements (14). The expansion required to supply this increased demand was made both in the electrolytic process and in a new high pressure catalytic process. Pilot plant studies conducted by Atlas Powder Company on the latter process, during the war, indicated a substantial increase in the rate of reaction compared with the electrolytic process, which is inherently slow.

In 1947 the production facilities of the Atlas Powder Company were completely converted to the catalytic process. This process is discussed by Porter (14). A flow sheet and a brief description of the process is presented in a more recent article (1). The catalytic process is continuous, in contrast to the batchwise electrolytic process. The operating pressure is reported to be about 125 atmospheres, but no indication is given as to the temperature employed.

The probable reasons for the conversion to the catalytic process, in spite of the large capital outlay required, were the prevailing low rates of the electrolytic process, the difficulty experienced in the control of product quality, and purifications problems. It is safe to say that some of these same problems may be attendant upon the operation of the newer process, to some extent. Although the rate of reaction is undoubtedly superior in the catalytic process, certain other problems would be expected to arise. Thus, the handling of high pressure hydrogen entails certain predictable difficulties as does the use of a catalyst.

If it were possible to make significant improvements in the electrolytic process, it is not unreasonable to believe that it could be

placed on a competitive basis with the catalytic process. Several modifications of the electrolytic process have been proposed recently by Emerson (15), which suggest the possibility of substantial amelioration.

The ideas proposed by Emerson are incorporated in a patent (15). Through more effective control of the process variables, by the methods suggested, it might be possible to obtain higher reaction rates than realized commercially and also to gain the added advantage of product quality control. A detailed study of the points presented in the Emerson patent comprises the experimental investigation reported in this paper.

Before discussing the experimental program and the results obtained, it is well to consider some of the important phases of electrochemistry in general and electro-organic reduction in particular. Thus, in the following sections the theory of electrolytic reduction will be considered with particular attention being given to electrode potential, depolarizing agents, electrode material, reduction of dextrose in alkaline solution, reduction of dextrose in acid solution and possible improvements in the electrolytic process.

Following the brief presentation of theoretical considerations and the survey of the electrolytic reduction of dextrose, the experimental program will be outlined.

Theory of Electrolytic Reduction

Electrode Potential.--The electrolytic reduction of an organic compound consists essentially of two steps (6). There occurs first the formation of atomic hydrogen at the cathode, either by direct discharge of hydrogen

ions or by interaction of other discharged cations with the water of the solution. Reaction of the active hydrogen with the organic compound comprises the second step. The organic compound thus reduced is termed a "depolarizer".

The rate of depolarization or reaction of the organic compound with active hydrogen at the cathode surface is dependent upon several factors. One such factor is the cathode potential, which is simply the potential existing between the reducing electrode and the solution in contact with it.

If a metal electrode is placed in a solution of its ions, a definite reproducible electrode potential is established which is dependent upon the nature of the metal and the concentration of the ions. If the potential is made infinitesimally more negative by an external source of e.m.f., ions will be discharged to form atoms on the surface of the electrode. Raising of the potential, i.e., making it more positive, results in solution of the metal to form ions. The equilibrium or reversible potential automatically established when the metal is placed in the solution is the potential at which discharge of the metal ions just begins to occur from the given solution.

The concept of the equilibrium potential applies equally well to substances which are gases, such as hydrogen or oxygen. Thus, the reversible electrode potential required to discharge hydrogen ions from a one normal sulfuric acid solution is -0.02 volts. However, in practice it is found that the potential required to cause the discharge of hydrogen ions at a finite rate is much greater than the reversible potential. This observed phenomenon is attributed to irreversibility

in the discharge of the ions and is called "polarization". The difference in the actual potential at which hydrogen ions are discharged and the reversible potential is called the hydrogen overvoltage.

The main difference between an electrode operating reversibly and one operating irreversibly is that in the former case the ions are fully discharged and removed as molecules at a rate not less than the rate at which the ions are brought up to the electrode. In the case of the irreversible electrode the ions are not removed at this rate until the potential has reached a value considerably in excess of the reversible potential. There is evidently a delay in one of the stages between the ions in solution and the hydrogen gas molecules (16).

The stages between the hydrogen ions in solution and the molecular hydrogen evolved as bubbles of gas may be enumerated as follows: (1) transfer and diffusion of H_3O^+ ions to the electrode diffusion layer; (2) transfer of these ions or protons through the diffusion layer to the electrode; (3) discharge of these ions or protons; (4) union of the resulting hydrogen atoms to form molecular hydrogen; and (5) evolution of molecular hydrogen as bubbles of gas (17).

Different investigators studying hydrogen overvoltage have developed theories to explain the observed phenomenon, which theories are based on one or another of these stages as being the cause of irreversibility. Of the stages mentioned above, (1) and (5) are generally considered to be of secondary importance. At one time there was much support for the view that (4), i.e., the formation of molecular hydrogen from hydrogen atoms, was the rate determining step. More recently stages (2) and (3) have been given a good deal of

consideration.

The essential result of all of the theories proposed to explain hydrogen overvoltage is that a given depolarizer should be reduced more rapidly at an electrode at which a high electrode potential prevails than at one exhibiting a low potential. In other words, the electrode potential may be considered to be an indication of the reducing power of an electrode with a given depolarizer and catholyte.

According to the older theories based upon stage (4) as the slow process, the cathode potential was considered to be governed by the concentration of atomic hydrogen, C_H, at the cathode, according to the relation

$$P = P_o + \frac{RT}{F} \ln \frac{C_H^+}{C_H} \qquad (1)$$

where P is the electrode potential, P_o is the reversible electrode potential, R is the ideal gas constant per gram mole (1.985 x 4.184 joules), T is the absolute temperature, F is the Faraday (96,500 coulombs) and C_H^+ the concentration of hydrogen ions (18). According to the law of Mass Action, the rate of reduction of the depolarizer should become greater as the atomic hydrogen concentration increases. However, as this increase occurs, in a catholyte of relatively constant hydrogen ion concentration, the cathode potential becomes greater, i.e., more negative.

More recent theories consider overvoltage to be due to the height of the potential energy barrier, which prevents the passage of an electron from the cathode to a hydrogen ion brought up to it by the current (19).

This view has been subjected to quantum mechanical treatment as well as mathematical analysis using Sterns's concept of the electrical double layer at the electrode surface (20).

The possibility that the transfer of protons to the electrode (Stage 2) is the slow process responsible for polarization has been investigated by Glasstone and coworkers (20).

The various theories of overvoltage are considered quite completely in the references cited. The point of interest in connection with the present discussion is the conclusion that the rate of reduction of a depolarizer is affected by the magnitude of the electrode potential, a high potential making for a high rate of reduction.

Depolarizing agents.--In general, if the reaction

$$H^+ + e \rightarrow H \qquad (2)$$

is more rapid than the reaction of the active hydrogen, H, with the depolarizer, there will be an accumulation of atomic hydrogen at the electrode surface. As this concentration becomes sufficiently high, the reaction

$$2H \rightarrow H_2 \qquad (3)$$

by which molecular hydrogen is evolved will take place. Molecular hydrogen under normal conditions has little or no reducing power and its evolution therefore represents a decrease in the reduction efficiency of the electrolytic cell.

As the rate of current flow through an electrolytic cell is

increased, the rate of formation of atomic hydrogen rises. As the current is increased, there is a point at which the depolarizer can not react with the atomic hydrogen as fast as it is formed and molecular hydrogen is evolved as a gas. The point at which bubbles of molecular hydrogen are first noticed corresponds to a certain electrode potential for a given electrode. Hydrogen evolution occurs at about this potential regardless of the depolarizer present. On the other hand, the current density, i.e., the current flow per unit of cathode area, at which evolution of hydrogen is first detected depends upon the nature of the depolarizer.

In Figure 1 current density-cathode potential curves are sketched for a catholyte containing a very active depolarizer (Curve I), for a catholyte containing a somewhat less active depolarizer (Curve II) and for a catholyte with no depolarizer (Curve III) (21).

In the absence of a depolarizer (Curve III), the potential rises rapidly from a to b. At b, visible hydrogen evolution occurs and the potential at this point is the so-called bubble overvoltage potential. Beyond b, hydrogen evolution occurs freely with little increase in potential. The slight current flow observed between a and b may be due to traces of depolarizer in the catholyte or diffusion of hydrogen from the cathode into the body of the solution.

When a depolarizer is present (Curve II), the atomic hydrogen formed is removed by the depolarizer until some current density, d, is reached where the rate of hydrogen formation exceeds that of removal by the depolarizer. At this point the potential is b', approximately the same as b.

With a very active depolarizer, the variation of cathode potential

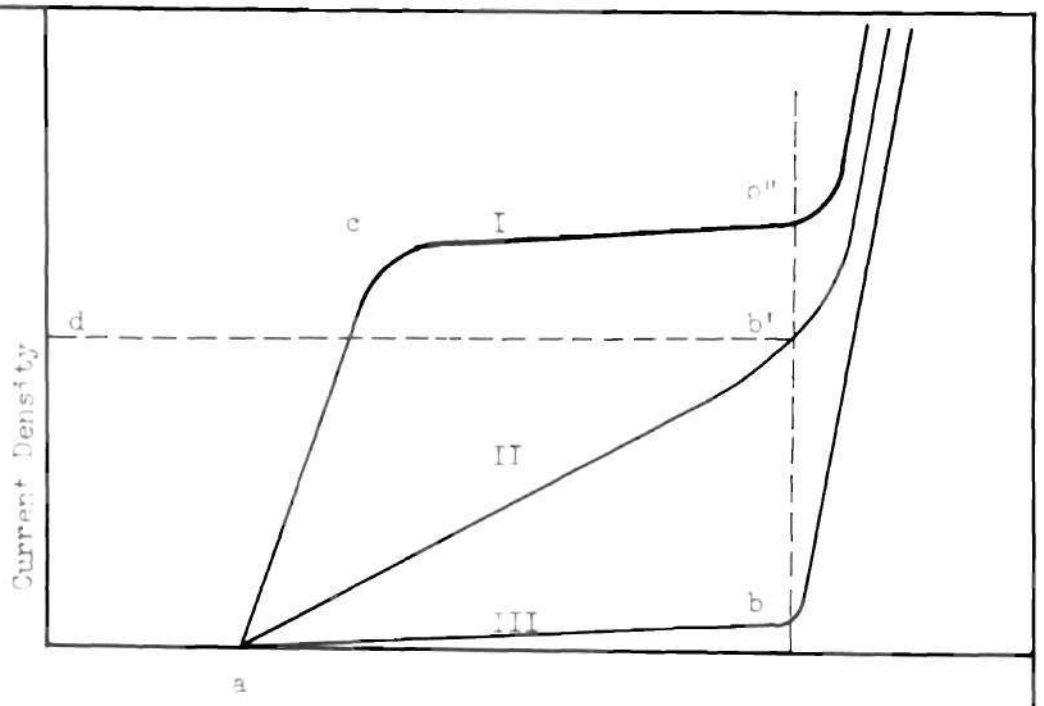


Figure 1. Variation of Cathode Potential with Current Density for a Given Depolarizer

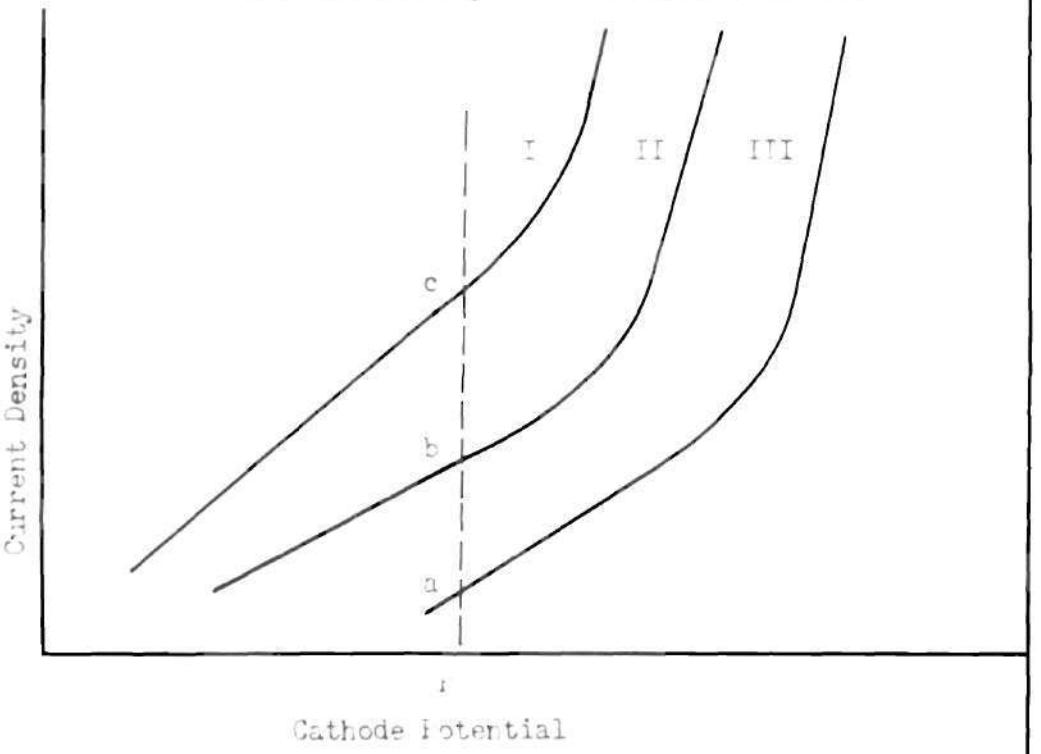


Figure 2. Effect of Electrode Material on Cathode Potential

with current density will be of the type illustrated by Curve III. In this case, as the current density is increased the cathode potential rises slowly until point c is reached. At this point the rate of diffusion of fresh depolarizer to the electrode surface is just equal to the rate of reaction with the atomic hydrogen formed. A slight increase in current density at this point increases the rate of formation of atomic hydrogen and in the absence of sufficient depolarizer for complete reaction, the electrode potential rises rapidly to the point b'' where hydrogen evolution occurs.

At any point on the three curves between a and b, a - b', or a - b'', the reduction efficiency is 100 per cent. In this range, one equivalent of hydrogen is liberated for each Faraday of electricity passing through the cell and this hydrogen is subsequently reacted with the depolarizer. Beyond the points b, b' and b'', where gaseous hydrogen is released, the efficiency is somewhat less than ideal.

The point a, which represents the static potential of the electrode, is dependent upon the nature of the electrolyte and electrode material. For the three cases just described, the static potential would not normally be the same.

Electrode material.—The preceding discussion of depolarizing agents indicated that, with a given cathode, hydrogen evolution is first noticed at about the same cathode potential in all cases. It is an experimental fact that different metals have widely different hydrogen overvoltages, i.e., different potentials corresponding to the points b, b' and b'' of Figure 1. The hydrogen overvoltages of the metals seem to rise in

order of their decreasing ability to catalyze the combination of hydrogen atoms to molecular hydrogen (22). In other words, as the order of catalytic power increases, the hydrogen overvoltage decreases.

It is desirable to use the highest electrode potential obtainable without the evolution of hydrogen in order to obtain 100 per cent reduction efficiency and high rates of reduction. In view of this, it is not difficult to understand why metals of high hydrogen overvoltage are selected for difficultly reducible compounds.

In Figure 2, the metals I, II and III have hydrogen overvoltages increasing in the order given (18). This means, in effect, that a higher cathode potential can be obtained with metal III before hydrogen is evolved than with the other two metals.

It is possible to obtain an electrode potential P with the three metals and given depolarizer, if the current densities are properly adjusted. Thus, by setting the current density of I at c, that of II at b and that of III at a, cathode potentials of P will be obtained in all three cases. In the absence of a catalytic effect by one or more of the metals, the reduction of a given depolarizer would be expected to proceed at the same rate. This expectation was realized by Lob and Moore (18) , who studied the reduction of nitrobenzene in an alkaline medium at a constant cathode potential P of about -1.5 volts, at six different cathode materials.

The results noted above are not always realized because of the catalytic action of some metals on the reduction process under consideration. Thus, in the electrolytic reduction of nitric acid to ammonia and hydroxylamine a low overvoltage copper cathode facilitated reduction to

93 per cent ammonia, while amalgamated lead, a high overvoltage cathode, resulted in only 17 per cent ammonia (18).

The condition of the electrode surface often has a marked effect on progress of a given reduction reaction. Roughening of the cathode surface amounts to increasing its surface area. For a given current flow the actual current density is actually lower for a roughened electrode than for a smooth one of the same size. The lower current density results in lower electrode potentials, as indicated by Figure 2, and consequent lower reaction rates would be expected. However, the catalytic effect of the increased surface area may actually cause the reduction rate to rise.

The conclusion to be drawn from the above discussion is that when a substance is a rather poor depolarizer, i.e., difficult to reduce electrolytically, such as materials containing a carbonyl group, an electrode material of high hydrogen overvoltage such as lead, thallium, mercury or amalgamated zinc should be employed.

Temperature.--In addition to the three factors already discussed, the temperature at which the electrolytic reduction is carried out has an important effect on the progress of the reaction. Because of the increase in the rate of the slow process causing polarization, as the temperature rises the hydrogen overvoltage is decreased. At the same time, increase of temperature causes an increase in the rate of diffusion of the depolarizer to the cathode and an increase in the rate of reaction of hydrogen with the depolarizer. The influence of temperature on the reduction reaction is determined by the relative importance of the

changes induced by the three factors mentioned above.

In the case of a reaction which requires only a moderate cathode potential an increase in temperature would probably cause an increase in reduction rate. When a poor depolarizer is involved and a high cathode potential required, an increase in temperature would be expected to decrease the reduction rate with a consequent decrease in efficiency.

Concentration of depolarizer.--The concentration of the depolarizer is quite frequently an important factor in determining the reduction rate. By increasing the concentration, or by agitation of the catholyte to bring the depolarizer into more intimate contact with the electrode surface, the reduction rate can sometimes be appreciably increased. In the case of an electrode with a very high surface area, such as a spongy or roughened electrode, agitation of the catholyte may improve results markedly because of the increased access of depolarizer to all of the active area.

Although there are other factors influencing the electrolytic reduction process, they are of less importance in considering the experimental work reported in this thesis. Consequently the discussion of the theory of electrolytic reduction will be terminated at this point and the specific case of the electrolytic reduction of dextrose will be considered.

Reduction of dextrose in an alkaline medium.--Parker and Swann (23) have reviewed the technical literature, through 1946, pertaining to the electrolytic reduction of dextrose. Only items of particular interest to the problem at hand will be referred to in the present paper.

In a series of experiments, Parker and Swann (23) investigated the influence of cathode material and structure on the reduction of dextrose, mannose and fructose in mildly alkaline solution. They found that high efficiency of reduction can be realized only at cathodes of soft metals which bear a close relationship to mercury in the periodic table. The active metals form an L in the table with mercury at the corner. Active metals in the vertical part of the L are zinc, cadmium and mercury. In the horizontal direction the active metals are bismuth, lead, thalium and mercury. Most of these metals have high hydrogen overvoltages, but tin, which has a very high overvoltage, was found to be only slightly effective. With the exception of tin, these results are in accord with the conclusions from the preceding discussion of the effect of the nature of electrode material on the rate of reduction.

Sanders and Hales (24) discuss the commercial electrolytic reduction process used until recently by the Atlas Powder Company. This process is performed batchwise. The usual values of operating conditions fall within the following limits:

Current Density.....1 to 2 amps./dm^2

Catholyte Temperature.....68 - 75°F.

Ratio of cathode area to catholyte volume....0.5 - 2.8 dm^2/liter

Alkalinity of catholyte.....0 - 20 gms. NaOH/liter

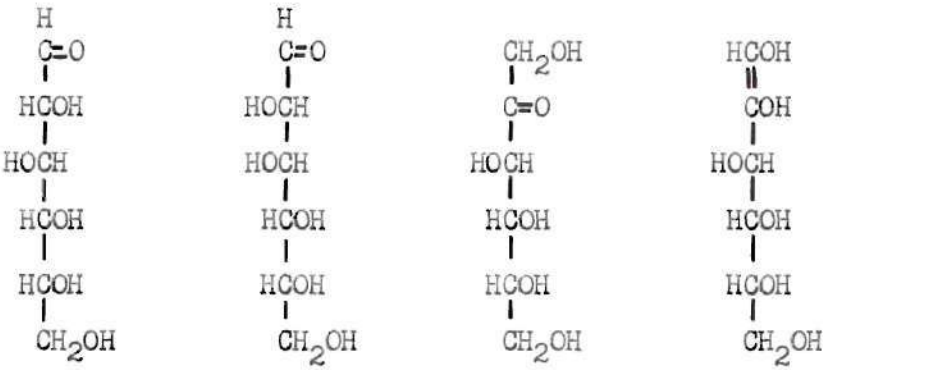
Initial sugar concentration.....300-500 gms./liter

Sodium sulfate concentration.....70-100 gms./liter

The sodium sulfate is added to the catholyte to provide suitable electrical conductivity. The quantity used is determined by economic considerations since the cost of electrical energy must be balanced

against the cost of separating the salt from the finished product. It has been found that in the absence of an alkali metal salt, such as sodium or potassium sulfate, no reduction occurs (25). It has also been observed that the rate of reduction is decreased markedly by the presence of small amounts of magnesium (26). Chromium is likewise deleterious, but small amounts of aluminum, nickel, copper and iron can be tolerated.

As indicated by the operating conditions cited above, the reduction is generally carried out in alkaline solution. A comprehension of the chemistry of dextrose in alkaline media is of value in understanding the selection of alkaline catholyte conditions. As is well known, dextrose in mildly alkaline solution undergoes the so-called Lobry de Bruyn-Van Ekenstein transformation (27). This transformation consists of the reciprocal interconversion of epimeric aldoses to their corresponding ketoses. For example, in the case of dextrose in saturated lime water at 35°C. the major equilibrium products may be represented as follows:



Other substances (probably Saccharinic acids) 3% (28)

Apparently, it is necessary that the dextrose undergo this enolization reaction in order that reduction may occur.

The presence of the 1-2 and 2-3 enolic forms has been established by Wolfrom and coworkers (29,30,31,32). By a series of extractions, crystallizations and derivative formations, these investigators were able to isolate from the product of the commercial electrolytic cell at mild alkalinity, the following substances: sorbitol, D-mannitol, allitol, a pentiol of unknown structure, 2-desoxysorbitol, a 2-desoxyhexitol of unknown structure and D,L-glucitol. Sorbitol would result from the reduction of either dextrose or fructose while D-mannitol could be formed by the reduction of either D-mannose or fructose. The 2-desoxysorbitol could arise from the reduction of the carbonyl in the open chain or keto form of D-fructose.

The possible enolic mechanism is presented in Figure 3. (29).

The alkaline environment necessary for the enolization reaction to occur has definite disadvantages, especially at high alkalinity and elevated temperatures. Under such conditions extensive degradation and transformation of the dextrose occurs (33). Part of the degradation results from contact with the oxygen of the air, with the production of aldonic and other acids with fewer carbons in the molecule (34). This degradation may be reduced by using floats of sponge rubber or paraffin to eliminate such contact (35).

A low operating temperature in the range 68-75°F. is necessary to keep the degradation within reasonable limits. In general, the reaction rate increases appreciably with temperature, but the ensuing degradation prohibits temperatures much higher than those stated. Creighton and Hales (10) found that somewhat higher temperatures could be employed if a compensating increase were made in the current density.

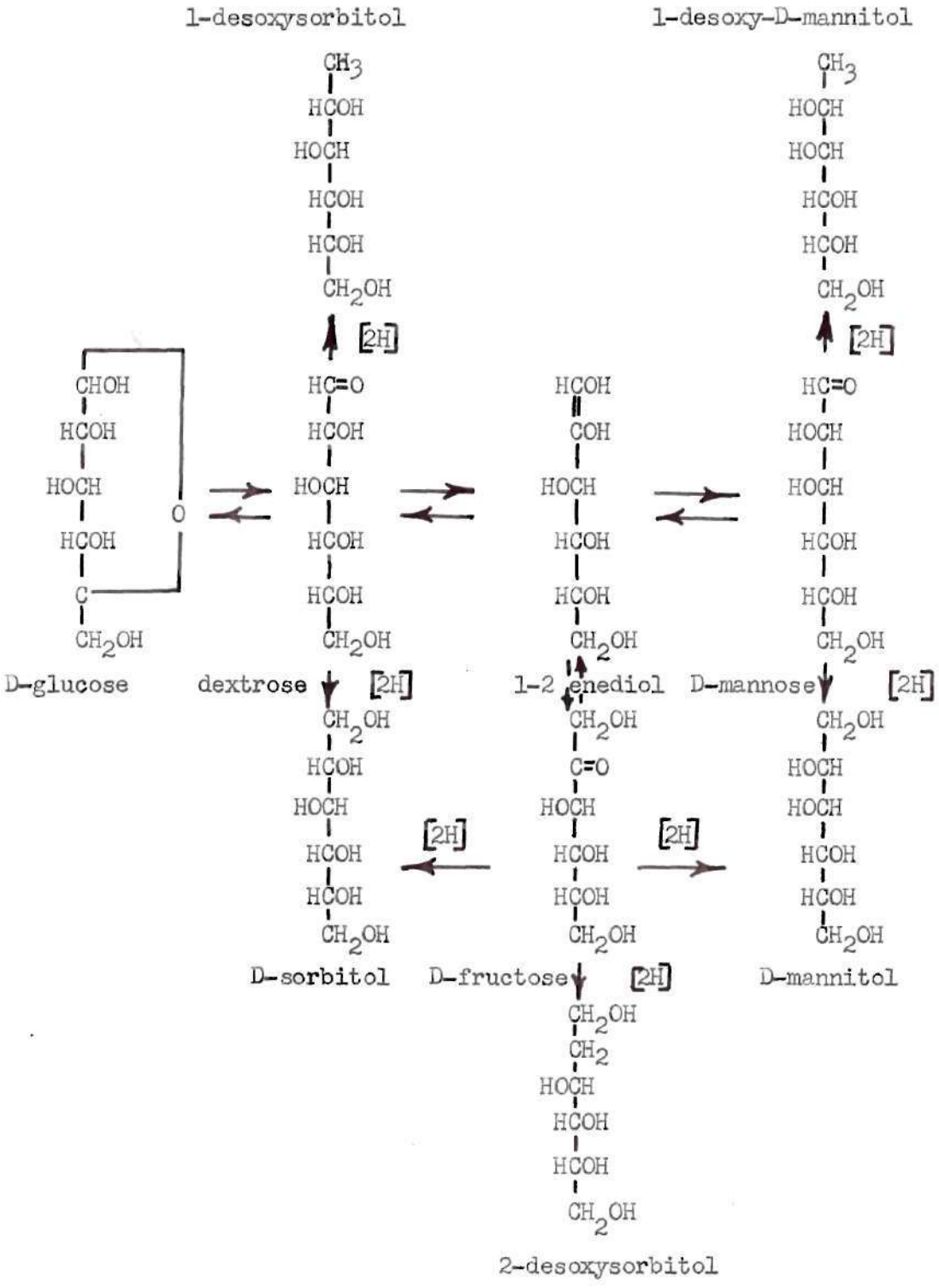


Figure 3. Enolic Mechanism of Sugar Interconversion Under Reducing Conditions

Their results are presented in the form of a correlation involving the variables temperature, current density, ratio of cathode area to catholyte volume and initial dextrose concentration.

The commercial electrolytic reduction unit consists of a cell, a tank, a cooler and a circulating pump arranged as shown in Figure 4.

The cell is a rectangular steel box, 13 feet long, 6 feet wide and 2 feet deep, internally lined with rubber. The cell box contains a series of diaphragm boxes containing the anodes. These diaphragm boxes are rectangular open-top ceramic containers which are 2 feet long, 2 feet deep and 3 inches wide. The cathodes are hung in the spaces between the diaphragm boxes and the catholyte is circulated by means of a pump.

The cooler is necessary to keep the temperature within the desired limits. The heat of reduction of dextrose to sorbitol is 110 B.T.U. per pound. This heat, along with heat absorbed from the surroundings and the pump as well as that due to the passage of the electric current through the cell, must be extracted in the cooler.

The cathodes used commercially are either amalgamated zinc or lead sheets, depending upon the conditions under which the reaction is carried out. Zinc cathodes result in more rapid reduction at low alkalinity (36).

The anodes are generally of sheet lead and become coated with lead peroxide in operation. The anolyte is a dilute solution of sulfuric acid, a concentration of 300 grams per liter being not uncommon.

At high alkalinity and elevated temperature a water insoluble deposit of organic material forms on the cathode side of the diaphragm. This deposit is generally removed from the diaphragm by washing with a

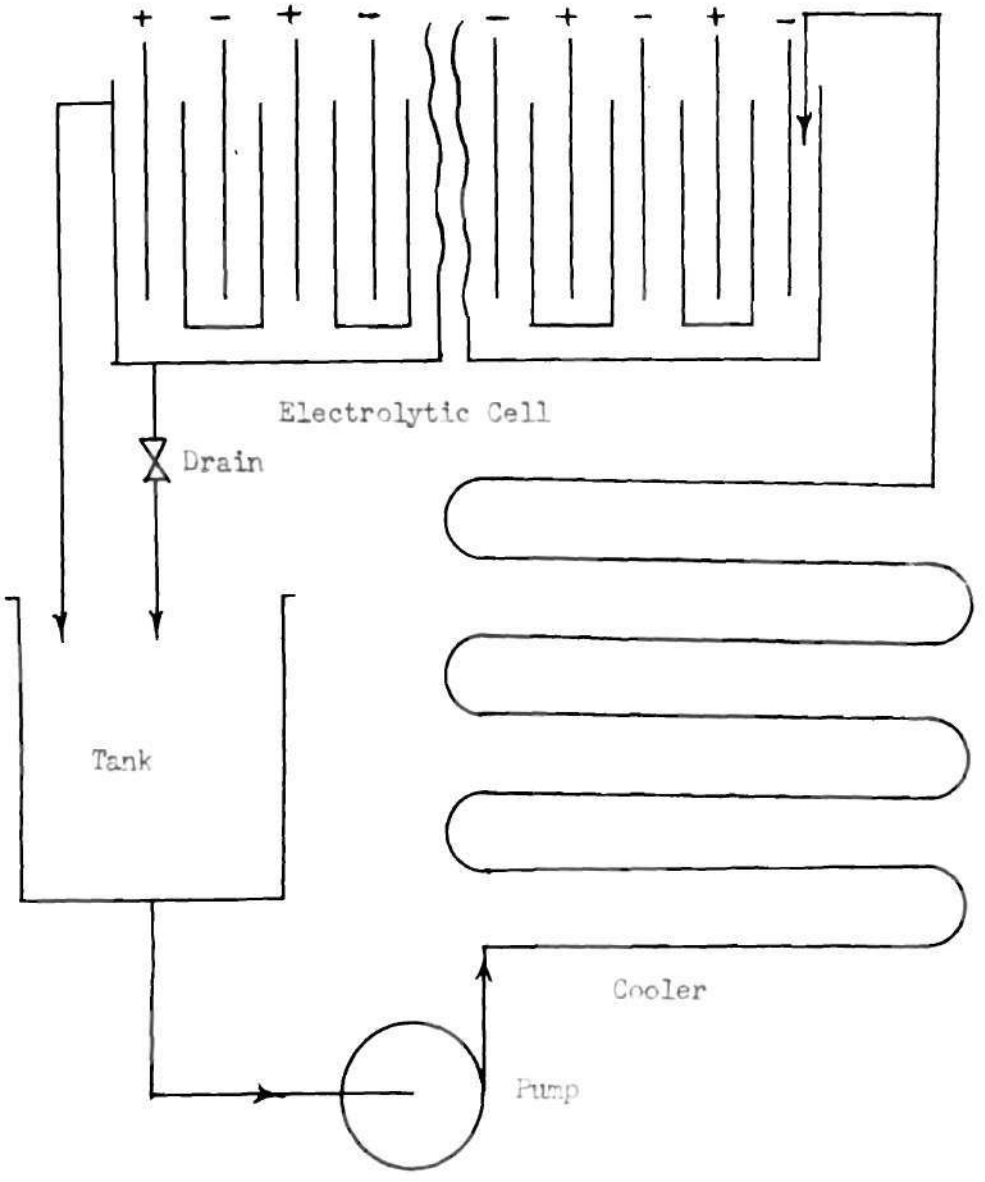


Figure 4. Arrangement of Equipment in Commercial Electrolytic Process for the Reduction of Dextrose

ketone.

During the course of the reaction there is a natural tendency for the catholyte to increase in alkalinity. This is due to the removal of hydrogen at the cathode at a rate greater than that at which hydrogen ions migrate into the catholyte under the influence of the electric current. The depletion of hydrogen ions must be compensated for by the addition of fresh acid to the catholyte or the catholyte pH rises to a point where extreme degradation occurs.

Reduction of dextrose in an acid medium.--Due to the extreme degradation of dextrose and the multitude of reduction products resulting at high alkalinity, control of the catholyte pH, when alkaline conditions are employed, is critical. The operating temperature must likewise be kept within certain narrow limits, depending upon the exact circumstances prevailing.

Since dextrose is most stable at a pH in the range between 3 and 4 (37), very little degradation would be expected to take place. In an attempt to avoid the difficulties encountered in alkaline catholytes, Hales (25) investigated the reduction reaction in an acid solution. He found that even in acid solutions of pH as low as 1.5, there was an alkaline film surrounding the cathode. Thus, dextrose molecules in diffusing through this film toward the cathode may undergo the enolization reaction mentioned previously and be reduced. An increase in temperature seems to have little effect on the reaction rate. It is probable that increased temperature, while tending to increase the rate of diffusion toward the electrode and the rate of combination of hydrogen and dextrose,

also tends to decrease the thickness of the alkaline film and lower the cathode potential. Thus, shorter retention time in the alkaline film and a lower cathode potential counteract the expected increase in reaction rate.

Possible improvements.--In an effort to improve the electrolytic process further, Emerson (15) has suggested certain unique modifications. The considerations involved are the result of an attempt to solve the problems attendant on the process by effective control of the alkalinity of the solution. Thus, the use of a buffer such as sodium hydrogen phosphate-sodium hydroxide, or other alkali salt of a weak acid whose anions do not interfere with the process, is recommended. By the use of catholytes buffered in this manner, it is possible to maintain a relatively constant pH at any point in the range 2.5 to 7.0.

As mentioned previously, an alkaline atmosphere is necessary for the reduction of dextrose to occur at a reasonable rate. In acid solution this alkaline environment is furnished by the pH gradient or alkaline film set up at the electrode surface. In order to insure the establishment of an alkaline film early in the reduction process Emerson suggests certain special procedures. One such technique is to add a small quantity of sodium hydroxide solution to the cathode surface. An alternate procedure is to start the reduction process with a very high current density of the order of 2 or more amps./dm^2, to cause the rapid depletion of hydrogen ions from the area surrounding the cathode.

A mercury-treated nickel electrode is recommended instead of the conventional amalgamated lead or zinc cathodes. This electrode combines

the high overvoltage characteristics of mercury and the strength of nickel. Unlike lead or zinc, the nickel electrode is not internally weakened by the mercury treatment, which takes place only on the surface.

In contrast to the low commercial operating temperatures, the temperature suggested for use in the modified process is 100 to 120°F.

As mentioned previously, there is a natural tendency for the pH of the catholyte to increase as the reduction proceeds due to the depletion of hydrogen ions. This depletion of hydrogen ions must be compensated for by the addition of acid by some means. Direct addition to the catholyte risks the possibility of disturbing the alkaline film on the cathode. In view of this possibility Emerson suggests the use of electroendosmosis of anolyte acid, i.e., bulk movement of anolyte acid through the pores of the diaphragm under the influence of the electric current, to accomplish this addition.

In all electro-organic reductions it is necessary to use a porous diaphragm to separate the catholyte from the anolyte. The purpose of this separation is to prevent re-oxidation of reduction products or oxidation of the initial reactant. The diaphragm must be of a material which not only is resistant to the solutions in the cell but which does not introduce any undesired contamination into the electrolytes. Furthermore, the permeability of the porous separation must be such that no appreciable diffusion of reactants occurs from the catholyte to anolyte, and yet it must pass ions freely to keep the electrical resistance of the cell as a whole within reasonable limits. For use in the modified process, an alundum (Al_2O_3) or similar diaphragm possessing a permeability of 5×10^{-5} darcys is recommended. A barrier of this type

is said to possess not only the characteristic mentioned above, but also is of such a nature that electroendosmosis can be induced through it.

Essentially all of the principal ideas embodied in Emerson's patent have been presented above. The specific conditions of operation recommended may be summarized as follows:

Catholyte Composition

200-325 gms./liter dextrose

$\frac{1}{2}$ - 2M NaH_2PO_4 (or other buffer salt)

NaOH to obtain desired pH

Catholyte pH.....2.5-7.0

Anolyte Composition

1 - 3M H_3PO_4

Electrodes

Anode....lead

Cathode....mercury-treated nickel or iron, oramalgamated zinc or lead

Operating temperature	100 - 120°F.
Current density	0-4 amps./dm^2
Ratio of cathode area to catholyte volume	15.4 dm^2/liter
Diaphragm permeability	5×10^{-5} darcys
Distance between anode and cathode	1.5-3.0 inches

As already stated, the ideas involved in these suggested modifications are incorporated in a patent. The results of seven runs under the suggested conditions are reported in this patent and are reproduced for ready reference in Table 46, APPENDIX II.

A detailed study of the suggested modifications comprised the

experimental phase of this thesis program. In the section immediately following, the experimental program is presented in detail.

Experimental Program

The commercial modifications of the electrolytic process for the reduction of dextrose, proposed by Emerson (15), seemed to offer real promise of significant improvements in the operation of the process. In view of the increasing importance of sorbitol, a study of these modifications was undertaken with particular attention being given to sorbitol production.

The first phase of the program consisted of exploratory runs to determine the relative position of the modified process with respect to existing processes, both electrolytic and catalytic. This work involved the determination of rates of reduction and current efficiencies as affected by current density and electrolyte composition.

In the major portion of the work a more detailed study was made of the variables affecting the reduction process itself in order to explain the results obtained from the preliminary investigation. Thus, the effects of cathode potential, catholyte pH, dextrose concentration, agitation and current density on the reaction rate were determined. Experiments were made in the same apparatus under conditions prevailing in industry to provide a means of evaluating the modified procedure.

With the exception of one run, the length of each experiment was limited to about eight hours, in order that a wide range of conditions could be studied. One run of twenty-four hours duration was made to establish a comparison with runs reported by Emerson (15).

EQUIPMENT

The experimental apparatus consisted of an electrolytic cell, controlled current power supply and various auxiliary components arranged as shown in Figure 18, which will be found in APPENDIX I, along with all other Figures and Tables referred to in this section. The individual components of the system are considered in some detail where such consideration seems warranted.

Electrolytic cell.—The electrolytic cell consisted of four essential parts, namely, the main container, the ceramic diaphragm, the electrode system and the supporting cover. In the case of a run made with an agitated catholyte, the agitating mechanism must be added to this list.

The cell container consisted of a 6 inch long by 3-3/4 inch wide by 5-3/4 inch deep Kodak hard rubber film tank.

The diaphragm used was constructed by cementing two flat porous plates between plexiglas spacers as shown in Figure 19. This procedure produced a very satisfactory diaphragm which exhibited an almost constant permeability from run to run. The permeability, determined from the flow of water through the diaphragm under a constant head, was calculated to be 1.67×10^{-6} darcys. The pore diameter calculated from this same information was 3.8 microns. Using an entirely different technique the Micromeritics Laboratory of the Georgia Tech Experiment Station determined the pore diameter to be 4.0 microns. The porosity was taken to be 0.35 based on Filtros Company descriptive literature. The porous plates,

furnished by the Filtros Company, were essentially $3Al_2O_3 \cdot 2SiO_2$.

It was originally intended that the diaphragms should be one piece, rectangular, ceramic boxes as used industrially. An attempt to have such diaphragms made for the scale of work carried out during this program indicated that they would be very costly and also rather unsatisfactory. To solve this problem, a program was undertaken to build diaphragms in the laboratory to suit the required specifications. Two lines of attack were followed. One of these was that of using porous plates with plastic spacers as already described. The other was to slip-cast a number of diaphragm boxes to the shape desired and fire the products at different temperatures to obtain a range of permeabilities. The facilities of the School of Ceramic Engineering, Georgia Institute of Technology, were used for this work. Although satisfactory results were obtained, the diaphragms of the first type mentioned were considered more desirable and consequently used in the experimental program. Table 14 shows the permeability as a function of firing temperature for the slip-cast diaphragms.

The electrodes used in the electrolytic cell were all of the size and shape shown in Figure 20 and were arranged as shown in Figure 21. The tabs of the electrodes were covered with a film of plexiglas to insure a constant exposed area in the solution. The anodes were cut from 1/8 inch thick sheets of chemical lead. The cathode was made from 1/8 inch thick pure nickel sheet and treated to provide a mercury surface. The treating procedure is described in the section entitled "Experimental Procedure".

The cell cover was made of 3/8 inch thick plexiglas with appropriate holes and slots cut to accomodate the electrode tabs, sample tubes, thermometers and the catholyte level indicator. When assembled, the transparent cover also served to hold the diaphragm in place in the cell.

Since the agitating device was used in only one run, no more than a brief description of it will be given. The agitator blades consisted of two thin horizontal plexiglas paddles, one on each side of the electrode, which were made to go up and down in the catholyte at a rate of about six cycles per minute. This reciprocating motion was supplied through a linear cam from a small A. C. motor.

The photographs in Figures 22, 23 and 24 show the assembly of the various parts of the cell just described. The burette tube shown on the top of the cell is part of the catholyte level indicating device. Contact between the catholyte and sensing element, which slides in this tube, is indicated by deflection of a galvanometer. The sensing element consisted essentially of two platinum wires separated by about 1/8 inch and placed in a circuit with a small battery, rheostat and galvanometer. When the wires touched the surface of the solution, a small current flowed and was indicated on the galvanometer. The results obtained with this arrangement were quite reproducible and could be translated in terms of the volume of catholyte. This information was necessary to calculate the absolute amount of dextrose in the catholyte from the concentration of a measured sample.

The volume of catholyte employed in all runs was 300 ml. The anolyte volume was generally about 1,250 ml. The active area of the cathode was 3 dm^2 in all cases and the ratio of cathode area to catholyte

volume was 10 $dm.^2$/liter.

Controlled current power supply.--In order to insure constant current density during any given run, the power supply shown in Figure 25 was constructed. This unit is unique in its ability to provide a constant flow of substantially ripple-free current under widely varying load conditions. It was designed by Dr. F. O. Nottingham of the School of Electrical Engineering and built by the author under his guidance. It is capable of supplying up to twelve amperes of controlled current at voltages as high as 60 volts.

The rectifier section of the unit consists of two C6J grid-controlled thyratron tubes and a heavy filter circuit. Grid control is accomplished by phase shifting of the thyratron grid voltage in a simulated saturable reactor. The D. C. winding of the reactor is supplied with the plate current from the 6SH7 pentode, which in turn is controlled by the plate current of the 1A5GT diode. The plate current in the 1A5GT control tube is dependent upon the filament temperature and therefore on the voltage impressed across the tube. The Ayrton shunt (A_1) comprises the regulating system of the unit by altering the voltage impressed upon the control tube.

The control system is a closed cycle and consequently has a tendency to "hunt". This tendency is eliminated by means of the "anti-hunt" circuit (AH).

The power supply was found to fill the need for a constant, ripple-free current very satisfactorily and is described here as an aid to others who may place the same requirements on a direct current supply

source.

Cathode potential measuring apparatus.--The equipment used for the measurement of cathode potentials is shown in Figure 26. In this case the potential of the cell consisting of the saturated calomel electrode and the cathode of the electrolytic cell was determined using a Leeds and Northrup potentiometer and potential divider.

Miscellaneous equipment.--The ammeters used for current measurement were Weston model 280, triple range D. C. instruments. The cell voltage was measured with a Weston model 301 voltmeter.

The pH measurements were made on a Beckman model H-2 line operated instrument.

The spectrophotometer used to explore the possibility of a spectrophotometric procedure for dextrose was a model B - Beckman instrument.

The photographs presented in Figures 27 and 28 show some of the assembled experimental apparatus.

EXPERIMENTAL PROCEDURE

Standard operating procedure.--A stock solution of 4 molar phosphoric acid was made up to be used as anolyte in all runs. Catholyte solutions were made up by adding the required amounts of alkali, buffer salt and sugar to a volumetric flask partially filled with water. The materials must be added in the order mentioned with thorough mixing between additions to prevent the degrading action of the caustic on the dextrose. After solution of all of the solid material, distilled water was added to bring the solution to the required volume.

In initiating a run, measured volumes of anolyte and catholyte were heated to slightly above the operating temperature and placed in the assembled cell. Prior to this the cell itself was placed in the heated water bath. The slight excess of heat put into the solutions was necessary to raise the temperature of the electrodes and diaphragm to the operating level. When the cell had been readied for use, the level of the catholyte was measured and current started through the cell at whatever rate was desired. Timing of the run was started as soon as the current flow began.

Samples of catholyte were removed periodically during the run for dextrose determinations and pH measurements. The probe of the electrode potential apparatus was carefully placed at the cathode surface for measurements every one-half hour or less. At the end of the run, samples of catholyte were analyzed for dextrose, sorbitol and

carbon content and the carbon in the anolyte was determined.

Temperature, catholyte volume, pH, cell voltage and cathode potential were recorded before each sample was taken and also at frequent intervals in between samples.

Investigation of electroendosmosis.--Where it was the purpose to study the extent of electroendosmosis in the electrolytic cell, no chemical analyses were made. Cathode potential and pH were measured much more frequently than in a standard run. The other features of the procedure were identical with those of a standard run.

Measurement of cathode potential.--The probe of the electrode potential apparatus was lowered to exactly the same point on the electrode surface for each measurement. After each reading the probe was removed to prevent interference with the electrolytic process by obscuring part of the electrode surface.

The e.m.f. measured by the potentiometer is that of a cell composed of the saturated calomel half-cell and the half-cell consisting of the cathode and the solution surrounding it. The negative terminal of the cell formed in this manner was found to be the cathode of the electrolytic cell. If the e.m.f. of the cell measured by the potentiometer is designated as E, and the single electrode potential of the saturated calomel half-cell by e_s, then the potential, P, of the mercury-treated nickel cathode in the electrolytic cell is given as:

$$P = e_s - E \quad \text{or} \quad P = 0.2415 - E \text{ volts}$$

The convention with regard to the sign of the electrode potential

may be stated as follows: The sign of the electrode potential is the same as the sign of the charge on the electrode. Thus, the sign of the charge on the metal is placed before the potential difference existing between the electrode and the solution in contact with it to obtain the electrode potential. This convention is the official standard of the American Electrochemical Society, the National Bureau of Standards and other scientific groups (38).

Cathode treatment.--The nickel electrode used in the electrolytic cell was treated to provide a mercury surface by the following procedure. The electrode was first etched with nitric acid and then placed in a bath of an acidic solution of mercuric nitrate. After a period of a few minutes the surface of the electrode acquired a shiny coating of mercury and was water washed and placed in use.

Storage of the electrode between runs in air or water causes a loss of the mercury coating and necessitates a treatment before each run. However, the treated electrode may be satisfactorily stored under mercury with no ill effects on the metal and the necessity for more than one initial treatment is thus avoided. During a run the mercury coating remains intact.

ANALYTICAL METHODS

In order to study the reduction process occurring in the electrolytic cell, it was necessary to employ various methods of quantitative analysis. An attempt was made to combine simplicity and accuracy in the procedures finally selected. The discussion in this particular section is intended to describe the methods used and to provide an estimate of the accuracy that can be expected from them. Where several competitive methods were investigated, the results obtained are presented here as an aid to other workers.

Determination of dextrose.--Three general methods were considered for use in the determination of dextrose. Two of these were standard methods, or modifications thereof. The two standard methods are dependent upon the reducing power of dextrose and the oxidation of dextrose by iodine. The third method was a spectrophotometric technique which depends upon the absorption of light by the pink solution produced when dextrose and carbazole react in concentrated sulfuric acid.

The method eventually selected for use in the experimental work was that of Lane and Eynon (39). This method involves the determination of the volume of sugar solution required to reduce completely a measured volume of alkaline copper solution. The end point is indicated by the reduction of methylene blue to methylene white when a slight excess of reducing sugar occurs.

Lane and Eynon determined the amount of dextrose required to

reduce a given volume of standard copper solution. These data were then presented as a table from which the concentration of a given sugar solution can be calculated from the results of a simple titration.

In the application of the analytical procedure to the determination of dextrose in the catholyte of the electrolytic cell, the following procedure was followed. One milliliter of catholyte was accurately measured into a 200 milliliter volumetric flask and distilled water was added to the mark. After thorough mixing, the volume of this solution required to reduce a mixture consisting of five milliliters of a solution containing 69.28 grams $CuSO_4 \cdot 5H_2O$ per liter, and five milliliters of a solution containing 346 grams Rochelle salt and 100 grams of sodium hydroxide per liter, was determined. In the titration procedure, all but about one milliliter of the sugar solution required for complete reduction was added to the flask containing the mixture mentioned above. The flask was then heated and after the liquid began to boil it was kept in moderate ebullition for two minutes. Without removing the source of heat three to five drops of methylene blue indicator were added and the titration completed in about one additional minute.

From the titration the concentration of sugar per liter is then

$$200 \times \frac{\text{Factor}}{\text{Titer}} = \frac{\text{gms. sugar}}{\text{liter}}$$

where the appropriate Factor is selected from the Lane and Eynon table for the titer obtained. A convenient table of Lane and Eynon Factors is given by Bates (40) for dextrose and other reducing sugars for which the

method is applicable.

Table 15 indicates the accuracy obtained with the Lane and Eynon method when known samples of dextrose were analyzed under conditions similar to those in the catholyte of the cell. The average error was less than 1 per cent.

The iodometric determination of dextrose was investigated using the methods of Willstäter and Schudel (41) and Kline and Acree (42). Since these methods were not used in the experimental work, the procedures will not be reported here. However, some of the results obtained are included in Table 16, where the three methods for the determination of dextrose are compared. Apparently the constituents of the buffered catholyte interfere with the reactions involved in this procedure.

The spectrophotometric technique was based mainly on the work of Gurin and Hood (43). This method depends upon the light absorption of the pink solution formed by the reaction of dextrose and carbazole in concentrated sulfuric acid. Although very low dextrose concentrations can be determined rather accurately, the procedure is more tedious and time consuming than the Lane and Eynon method. Again, the procedure is not repeated here but results obtained are reported in Table 16. In addition, a curve of concentration versus absorbance (Figure 29) and a series of curves of absorbance versus wavelength with concentration as parameter (Figure 30) are presented. The experimental data from which these figures are constructed are recorded in Table 17. The absorbance maximum observed at 535 m u is not affected by the presence of sorbitol, mannitol or inorganic compounds such as NaH_2PO_4, NaOH, etc. The presence

of these substances in a sample therefore does not interfere with the utility of the method for dextrose determination.

The study of the three methods just described indicated that the Lane and Eynon method is reliable, simple to use and accurate to within 1 per cent. Data on the other methods are included as a matter of interest.

Determination of sorbitol.--The sorbitol content of the catholyte liquor was obtained by separating the sorbitol from a one cc. sample by chromatographic adsorption, elution of the sorbitol zone and determination of the sorbitol content of the eluate.

The chromatographic technique used is the result of the work of Wolfrom and Coworkers (44,45,46,47) and is essentially that suggested by the Board of Standards of the Toilet Goods Association. (48). The determination of the sorbitol content of the eluate was accomplished by oxidation with periodic acid (49). The description of the procedure follows.

One cc. of catholyte is chromatographed on a 38 mm. by 230 mm. column containing 90 grams of a mixture of five parts by weight of Florex XXX (sold by the Floridin Company of Warren, Pennsylvania) to one part by weight of Celite 545 (produced by Johns-Manville of New York). Three hundred and twenty-five ml. of 85 per cent isopropyl alcohol are used as developer. The developing process required from three to eight hours, depending upon the method used to pack the column. The column is extruded after development and streaked several times with an alkaline permanganate solution (1 gm. $KMnO_4$, 10 gm. NaOH, water to make 100 ml.). After streaking and isolation of the sorbitol zone,

which in the present case was the top zone, the section of extruded column containing the sorbitol zone is scraped free of the streak marks and returned to the chromatographic tube. The column is then eluted with 200 ml. of distilled water. The filtrate thus obtained is diluted to 500 ml. in a volumetric flask.

A 25 ml. aliquot of the solution in the 500 ml. flask is measured into a small beaker. The solution is then allowed to simmer slowly until about one half of it remains, in order to remove any isopropanol present. After the addition of 10 ml. of 0.05 M HIO_4, the solution is heated to boiling and immediately cooled to room temperature. A slight excess of powdered sodium bicarbonate is added and then 10 ml. of 10 per cent KI solution are introduced. The solution is then titrated with 0.02 N sodium arsenite solution to starch end point. A blank is run using the same procedure and the sorbitol content is calculated according to the relation

$$\frac{\text{grams sorbitol}}{\text{liter of catholyte}} = 200(\text{ml. 0.02 N sodium arsenite required by blank - ml. required by sample}) \times 1.822(.02)$$

It is possible to determine the pyridine number of materials containing sorbitol (36), but this is a tedious process and results in only a relative index of sorbitol content. The phenylhydrazine test may be used for sorbitol determination, but it is rather complicated and time consuming. The combination of chromatographic adsorption and periodate oxidation affords a relatively simple and acceptably accurate method.

The overall procedure for sorbitol determination is estimated to give results within $\pm$ 3 per cent of the true values. Table 18 presents

the data obtained during the exploratory investigation of this method.

Determination of carbon.--In order to measure the extent of sugar losses by diffusion from the catholyte to the anolyte, it was necessary to determine the total carbon content of both anolyte and catholyte at the end of each run. The method used consisted of oxidation of a given sample with a chromic acid-sulfuric acid mixture and the subsequent absorption of the liberated carbon dioxide in a weighed ascarite bulb. The carbon content of the sample was calculated from the increase in weight of the absorption bulb. The method is essentially that of Pollard and Fosbee (50) and Adams (51).

For carbon determinations on the catholyte, one ml. of sample was used with 10 ml. of chromic acid solution containing 339 grams CrO_3 per liter, and 50 ml. of H_2SO_4 (Sp. gr. 1.83-1.84). The reaction mixture was heated for 1.5 hours, the heating being more vigorous as the determination proceeded. During the test, a steady stream of air, free of carbon dioxide, was passed through the apparatus. The total carbon in the catholyte is then

$$(\text{gm. of } CO_2 \text{ absorbed})\left(\frac{12}{44}\right)\left(\frac{\text{volume of catholyte in ml.}}{1 \text{ ml. sample}}\right) = \text{gm. C in catholyte}$$

The carbon determination on the anolyte was made in exactly the same manner except that a five ml. sample was used, and five ml. of chromic acid solution containing 680 gm. of CrO_3 per liter was employed. The larger sample was necessary because of the lower carbon content of the anolyte.

In a series of exploratory tests the maximum error in the determination of known samples was 3 per cent. The overall carbon balances

on the cell, Table 1, indicate recoveries within this limit of error.

Sampling techniques.--The estimated accuracy of the dextrose determination includes any error involved in obtaining the sample. It was found that indiscriminate sampling of the catholyte during a run caused substantial variation in the dextrose found by analysis from the dextrose found if the cathode compartment contents were well-mixed. This indicates a concentration gradient within the catholyte. It is obviously impossible to mix the catholyte uniformly before removing a sample, because of the disturbing effect on the reduction process. However, by carefully taking samples of equal volume at different distances from the cathode and analyzing the mixture of these samples, results were obtained which duplicated those obtained by analyzing a sample of mixed catholyte. This technique was used for removing all samples from the catholyte. A hypodermic needle and syringe were used to extract the volume required for analysis. Since the concentration of samples extracted from the catholyte were representative of the average concentration of the bulk of the solution, it is logical to assume that the pH of these samples should represent the average pH of the bulk catholyte. In view of the presence of the buffer in the solution this statement is further substantiated. Thus, the error in measurement of the pH of the bulk catholyte is not much greater than the error inherent in the pH meter employed. The instrument used was a model H-2 Beckman line operated meter which can be easily read to 0.05 pH unit. The error in measurement of catholyte pH is estimated to be less than this value.

Concerning the measurement of electrode potential no statement can be made except that the results are reproducible to about 0.005 volts.

The relative accuracy of the two procedures of electrode potential measurement, i.e., direct and commutator methods, is still an open question. Since relative values of cathode potential are of interest in the present case, the data can be considered quite reliable.

Although the measurement of current is rather unrelated to analytical methods, it will be considered at this point to enable the reader to appraise the accuracy of all the measuring and analyzing techniques at one time. During the early part of the experimental program a copper coulometer was used to measure the total equivalents of current which passed through the cell during a run. By placing an accurate ammeter in series with the coulometer it was found that the total current flow, as calculated from the ammeter reading, was never more than 0.5 per cent in error. The current flow was held constant during these test periods by the controlling circuit of the power supply. An ammeter could not be used in a case where the current flow varied during the progress of the run, without exact knowledge of this variation.

From the preceding discussion one may draw the conclusion that the maximum error of the analytical methods and various measurements is as listed below:

Dextrose determination	± 1.0 %
Sorbitol determination	± 3.0 %
Carbon determination	± 3.0 %
Current measurement	0.5 %
pH measurement	0.05 pH unit
Cathode potential measurement	0.005 volt

RESULTS

The reliability of the data recorded during the course of the experimental work is considered in the "Discussion of Results" under the heading "Reliability of Experimental Data". Information necessary to illustrate the factors discussed is supplied by Tables 1 and 2 and by Figure 5, which indicates the reporducibility of results.

Certain data are summarized to provide a general view of the results obtained. These data are presented in tabular form in Tables 3 - 8. The conversion of dextrose to sorbitol is indicated in Table 3. Table 4 shows the effect of current density on the rate of dextrose disappearance, while the current efficiencies and per cent reduction for runs numbered 7 - 35 are presented in Table 5. The rates of dextrose disappearance at 1.0 amps./dm^2 for unbuffered acid, buffered acid and unbuffered alkaline catholytes are given in Table 6. In Table 7, the dextrose disappearance during a long run is recorded. Table 8 shows the effect of buffer salt concentration on the rate of dextrose disappearance.

In Tables 9 - 12 and Figures 5 - 17 data are presented which permit analysis of the mechanism of the reduction reaction. Table 9 shows the effect of cathode potential on the reaction rate. The conversion of dextrose to sorbitol as affected by cathode potential, pH and current density is presented in Table 10. In Table 11 the effect of dextrose concentration on the reaction rate is shown and in Table 12

"apparent", "actual" and "sorbitol" efficiencies, to be defined later, are presented for runs 22 - 35.

Figure 5 illustrates the reproducibility of data, as already stated, and also the effect of catholyte agitation. In Figure 6 the effect of high current density preparatory periods of various duration for solutions at high acid pH are shown. In Figure 7 the same information is given for solutions of lower pH. Figure 8 presents the variation of reaction rate with cathode potential and Figure 9 illustrates the effect of catholyte pH on the reaction rate. The variation of cathode potential with catholyte pH is depicted in Figure 10. The effect of pH on reaction rate when a preparatory high current density period is employed is shown in Figure 11 while Figure 12 shows the same effect for runs employing no high current density preparatory period. Figure 13 shows the effect of pH, current density and dextrose concentration on cathode potential and Figure 14 shows the whole range of data from which Figure 13 was constructed.

The cathode potential and dextrose concentration during a twenty-four hour reaction period are shown in Figure 15. Figure 16 presents the data for the electroendosmosis of 4 M H_3PO_4 through the electrolytic cell diaphragm and Figure 17 provides the same information for 2 M H_3PO_4.

An effort to compare the modified process and the conventional electrolytic process from a standpoint of raw materials cost is summarized in Table 13.

Tables and Figures not pertinent to the discussion in the following section are placed in APPENDIX I in the same order in which they are

mentioned in other sections of the thesis. Those which have just been described will be found immediately following.

Table 1. Distribution of Carbon* at Completion of Runs

Run No.	Run Length (hrs.)	Carbon in Anolyte (%)	Carbon in Catholyte (%)	Carbon Removed in Samples (%)	Carbon Recovery (%)
22	8.083	7.40	89.60	2.40	99.4
23	8.0	7.10	90.20	1.50	98.8
24	8.417	5.45	90.60	2.35	98.4
25	8.0	4.77	93.60	1.83	100.2
26	8.417	6.54	94.10	1.36	102.0
27	8.0	4.91	91.30	1.59	97.8
28	8.417	7.57	90.90	2.03	100.5
29	8.417	5.80	89.30	2.40	97.5
30	8.417	6.25	89.10	2.45	97.8
33	24.0	17.60	77.60	2.20	97.4
34	8.0	6.20	91.50	1.20	98.9
35	8.0	5.10	96.20	1.00	102.3

*Expressed as per cent of original carbon in catholyte.

Table 2. Comparison of Calculated Current Efficiencies With Those Reported in Emerson Patent.*

Run No.	Reported C.E.	Calculated C.E.	Ratio of Calculated C.E. to Reported C.E.
1	43	29.8	0.694
2	52	20.8	0.400
3	55	19.3	0.352
4	66	48.2	0.732
5	50	38.3	0.766
7	43	20.8	0.484

*Calculated as illustrated by sample calculation in Appendix III.

Table 3. Conversion of Dextrose to Sorbitol

	Run No.	Time (hrs.)	Dextrose Disappearance (g.)	Sorbitol formed (g.)	Conversion of Dextrose to Sorbitol (%)
Unbuffered Acid Catholyte	34	8.00	32.45	19.80	61.0
Buffered Acid Catholyte	22	8.08	28.94	17.00	58.8
	23	8.00	34.95	20.30	58.0
	24	8.42	41.75	22.80	54.6
	25	8.00	27.69	13.50	48.8
	26	8.42	20.10	6.67	33.2
	27	8.00	16.08	5.82	36.2
	28	8.42	30.12	14.50	48.2
	29	8.42	23.40	14.85	63.5
	30	8.42	38.91	20.10	51.8
	33	24.00	65.17	22.60	34.7
Alkaline Catholyte	35	8.00	41.56	28.10	67.5

Table 4. Effect of Current Density on the Rate of Dextrose Disappearance

	Run No.	Current Density (amps./dm^2)	Time (hrs.)	Reduction (%)
Unbuffered Acid Catholyte	34	1.00	8.00	33.4
Buffered Acid Catholyte	29	0.45	8.42	24.0
	16	0.65	8.42	40.3
	18	0.65	8.33	30.4
	19	0.65	8.42	31.4
	22	0.65	8.08	29.6
	23	0.65	8.00	35.9
	24	0.65	8.42	42.0
	25	0.65	8.00	28.4
	26	0.65	8.42	20.5
	27	0.65	8.00	16.5
	33	0.65	24.00	66.5
	9	0.81	8.00	20.4
	10	0.81	8.00	17.2
	11	0.83	8.00	23.8
	12	0.81	8.00	22.3
	15	0.80	8.42	29.9
	7	1.05	8.00	18.8
	8	1.02	8.00	18.1
	28	1.00	8.42	30.7
	30	1.25	8.42	39.4
Alkaline Catholyte	35	1.00	8.00	42.8

Table 5. Current Efficiency and Per Cent Reduction for Runs Nos. 7-35

	Run No.	Reduction (%)	Current Efficiency* (%)
Unbuffered Acid Catholyte	34	33.4	40.4
Buffered Acid Catholyte	7	18.8	20.2
	8	18.1	19.9
	9	20.4	30.1
	10	17.2	25.7
	11	23.8	31.7
	12	22.3	33.2
	15	29.9	38.4
	16	40.3	54.0
	18	30.4	51.5
	19	31.4	52.4
	22	29.6	52.7
	23	35.9	66.7
	24	42.0	66.6
	25	28.4	52.9
	26	20.5	31.9
	27	16.5	31.1
	28	30.7	33.1
	29	24.0	50.2
	30	39.4	35.1
	33	66.5	39.6
Alkaline Catholyte	35	42.8	51.6

*Calculated from dextrose disappearance.

Table 6. Rate of Dextrose Disappearance at a Current Density of 1.0 amps./dm^2

	Per cent of Original Dextrose Disappeared				
Time-hours	0	2	4	6	8
Unbuffered Acid Catholyte (Run No. 34)	0	12.7	21.7	27.2	33.4
Buffered Acid Catholyte (Run No. 28)	0	10.8	17.8	23.9	29.9
Alkaline Catholyte (Run No. 35)	0	14.0	22.9	33.5	42.8

Table 7. Dextrose Disappearance During a Long Run

	Time-hours	Per Cent of Original Dextrose Disappeared
Run No. 33	0	
	3	18.9
	7	30.2
	11	40.9
	15	50.6
	20	59.6
	24	66.5

Table 8. Effect of Concentration of Buffer Salt on Rate of Dextrose Disappearance

Time-hours	Per Cent of Original Dextrose Disappeared							
	0	0.5	1.0	2.0	3.0	4.5	6.0	8.0
1 M NaH_2PO_4 (Run No. 9)	0	4.0	7.4	10.5	11.5	14.3	17.5	20.4
1.3 M NaH_2PO_4 (Run No. 12)	0	6.7	7.8	10.4	12.2	15.2	18.6	22.3
2 M NaH_2PO_4 (Run No. 11)	0	10.6	14.4	16.2	17.6	19.5	21.4	23.8

Table 9. Effect of Cathode Potential on Reaction Rate

Run No.	Time Interval From (hrs.)	To	Dextrose Reacted Per hour (grams)	Cathode Potential (volts)
29	5.0	8.42	0.821	-1.2385
27	2.0	8.00	0.742	-1.2405
26	2.0	4.00	0.878	-1.2635
22	3.5	8.08	2.016	-1.3685
30	2.0	5.00	2.118	-1.3765
28	5.0	8.42	2.240	-1.4205
24	2.0	5.00	2.887	-1.4460
25	5.0	8.00	2.977	-1.4605
23	4.0	6.00	3.080	-1.4885
24	6.0	8.42	3.417	-1.4935

Table 10. Conversion of Dextrose to Sorbitol as Affected by Cathode Potential, pH and Current Density

Run No.	Current Density (amps./dm^2)	Approximate pH Range	Per Cent of Reacted Dextrose to Sorbitol	Approximate Cathode Potential* Range
29	0.45	6.2-6.6	83.5	1.426-1.480
22	0.65	5.9-6.6	78.3	1.600-1.635
23	0.65	6.2-6.8	72.4	1.620-1.730
24	0.65	6.1-6.7	62.8	1.610-1.740
25	0.65	5.7-6.6	58.5	1.644-1.725
27	0.65	4.9-5.2	51.4	1.470-1.489
26	0.65	4.5-5.1	48.7	1.507-1.565
33	0.65	6.4-6.7	47.1	1.502-1.592
28	1.00	5.7-6.1	64.0	1.610-1.680
30	1.25	5.8-6.9	61.4	1.543-1.746
34	1.00	1.7-2.3	75.0	1.805-1.824
35	1.00	10.0-10.3	77.0	1.760-1.820

*Cathode Potential indicates the actual potentiometer reading of the cell consisting of the saturated calomel electrode and the cathode of the electrolytic cell.

Table 11. Effect of Dextrose Concentration on the Reaction Rate during Run 33

Time Interval From	To	Concentration Change (g./l.)	Average Rate of Change (g./l./hr.)	Average Concentration during interval (g./l.)	Average Cathode Potential during interval (volts)
6	9	27.5	9.17	221.25	-1.3525
9	12	25.5	8.50	194.75	-1.3685
12	15	22.0	7.33	171.00	-1.3825
15	18	19.0	6.33	150.50	-1.3935
18	21	17.0	5.67	132.50	-1.4035
21	24	15.0	5.00	116.50	-1.4135

Table 12. Apparent, Actual and Sorbitol Current Efficiencies for Runs Nos. 22 thru 35

Run No.	Current Density (amps/dm.^{2})	pH	Cathode Potential* (volts)	Apparent Current Effcy. (%)	Actual Current Effcy. (%)	Sorbitol Current Effcy. (%)
Unbuffered Acid Catholyte						
34	1.00	1.7-2.3	1.805-1.824	40.4	32.8	24.3
Buffered Acid Catholyte						
29	0.45	6.2-6.6	1.426-1.480	50.2	38.1	31.4
26	0.65	4.5-5.1	1.507-1.565	31.9	21.6	10.6
27	0.65	4.9-5.2	1.470-1.489	31.1	21.9	11.0
25	0.65	5.7-6.6	1.644-1.725	52.9	44.0	25.7
22	0.65	5.9-6.6	1.600-1.635	52.7	39.5	30.7
24	0.65	6.1-6.7	1.610-1.740	66.6	57.9	36.3
23	0.65	6.2-6.8	1.620-1.730	66.7	53.4	38.7
28	1.00	5.7-6.1	1.610-1.680	33.1	24.0	15.7
30	1.25	5.8-6.9	1.543-1.746	35.1	29.6	17.9
Alkaline Catholyte						
35	1.00	10.0-10.3	1.760-1.820	51.6	45.5	34.5

*Cathode Potential indicates the actual potentiometer reading of the cell consisting of the saturated calomel electrode and the cathodeof the electrolytic cell.

Table 13. Relative Costs of Commercial and Modified Electrolytic Processes for the Reduction of Dextrose*

From the standpoint of materials required, the following comparison may be made:

Basis: 1 liter of catholyte, 1 liter of anolyte

Modified Process

325 gms. dextrose @ $17.75/100 lbs.	-	$0.0718
120 gms. NaH_2PO_4 @ $8.15/100 lbs.	-	$0.0215
30 gms. NaOH @ $3.62/100 lbs.	-	$0.0024
245 gms. H_3PO_4 (2.5M) @ $9.70/100 lbs.	-	$0.0524
	Total	$0.1481

Commercial Process

325 gms. dextrose @ $17.75/100 lbs.	-	$0.0718
75 gms. Na_2SO_4 @ $2.00/100 lbs.	-	$0.0033
300 gms. H_2SO_4 @ $1.05/100 lbs.	-	$0.0069
	Total	$0.0820

*All price data obtained from Chemical Market Prices sections of Chemical and Engineering News, March 3, 10, 17, 24 (1952).

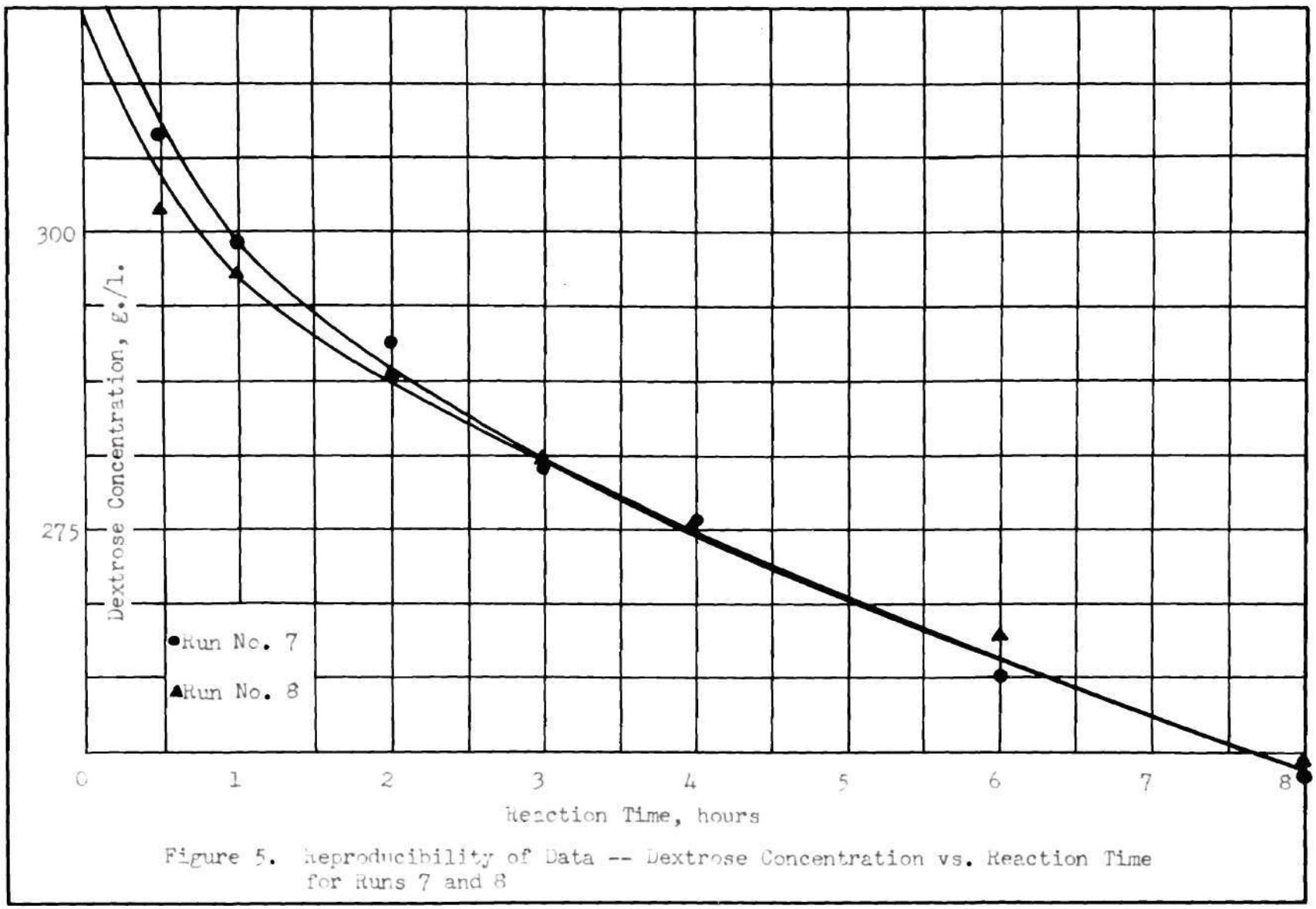


Figure 5. Reproducibility of Data -- Dextrose Concentration vs. Reaction Time for Runs 7 and 8

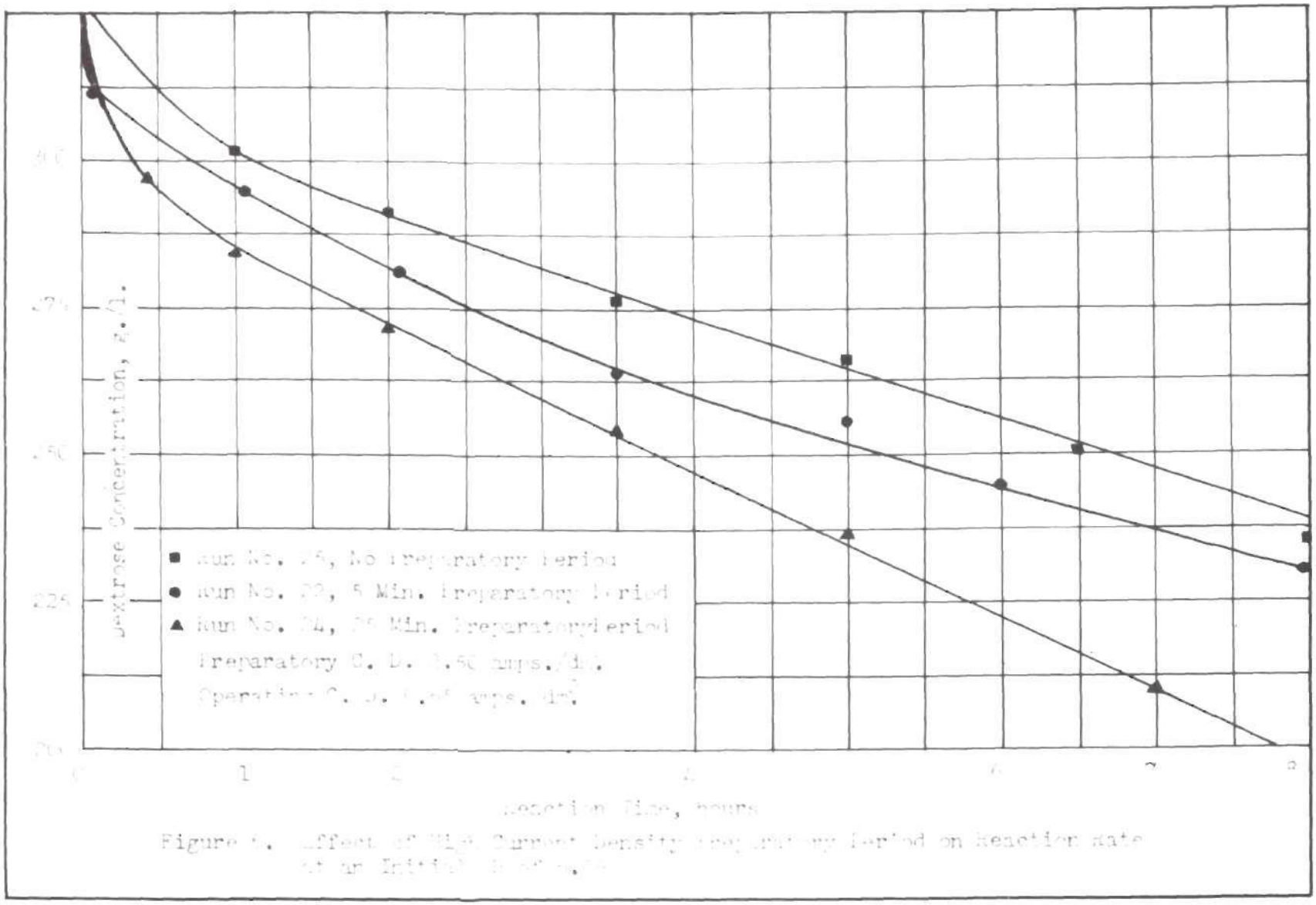


Figure 4. Effect of High Current Density Preparatory Period on Reaction Rate at an Initial [illegible] g./l.

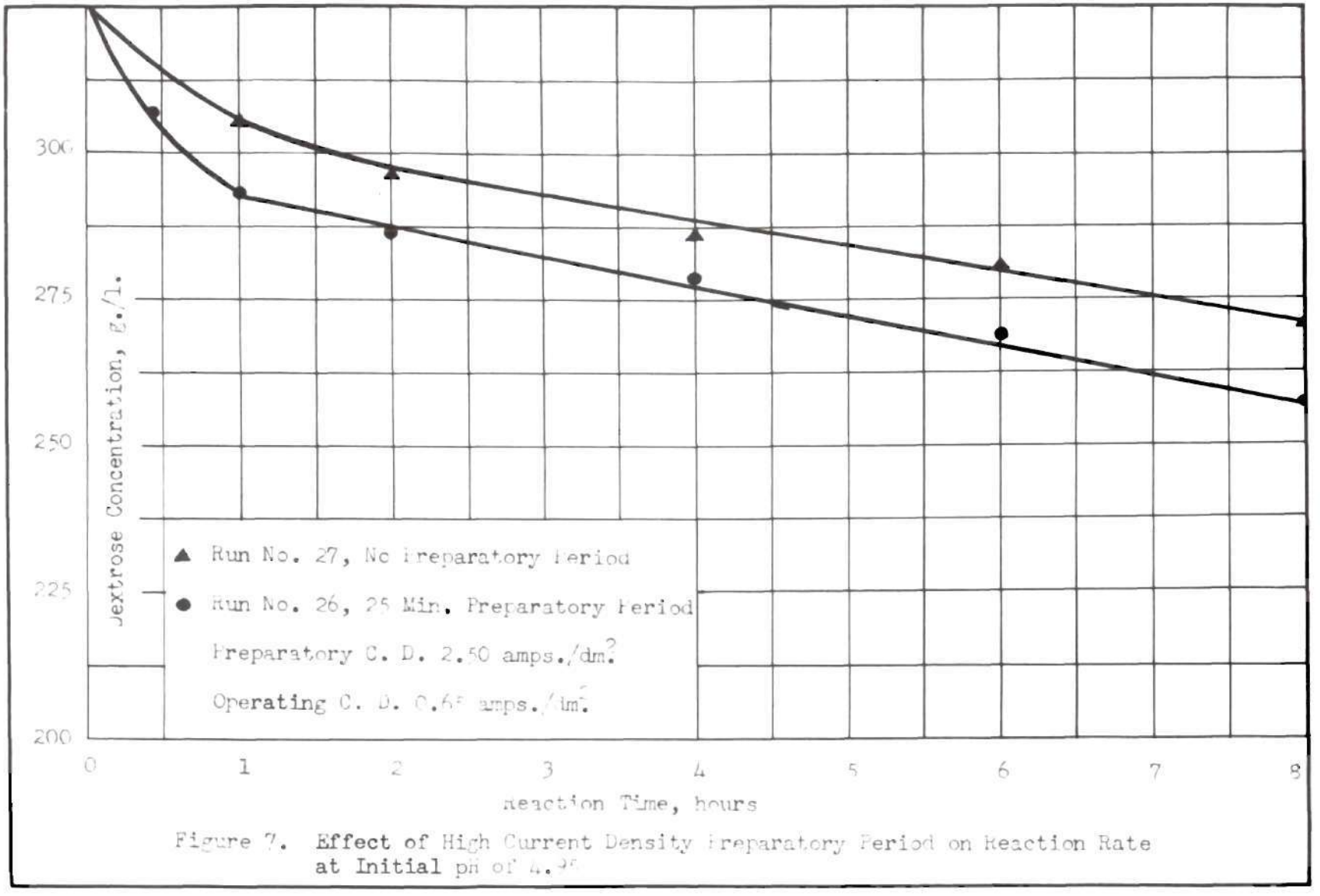


Figure 7. **Effect of High Current Density Preparatory Period on Reaction Rate at Initial pH of 4.2**

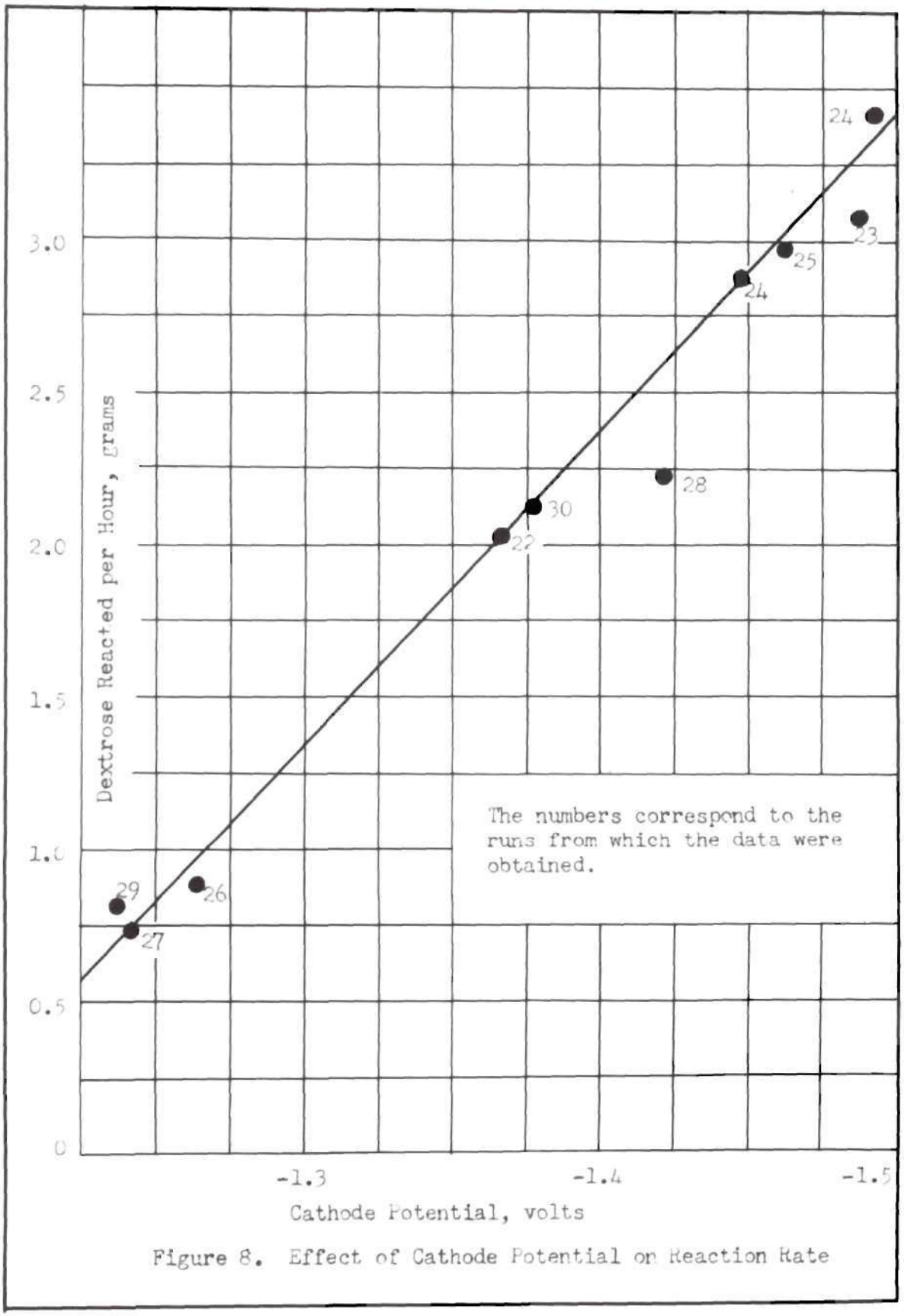


Figure 8. Effect of Cathode Potential on Reaction Rate

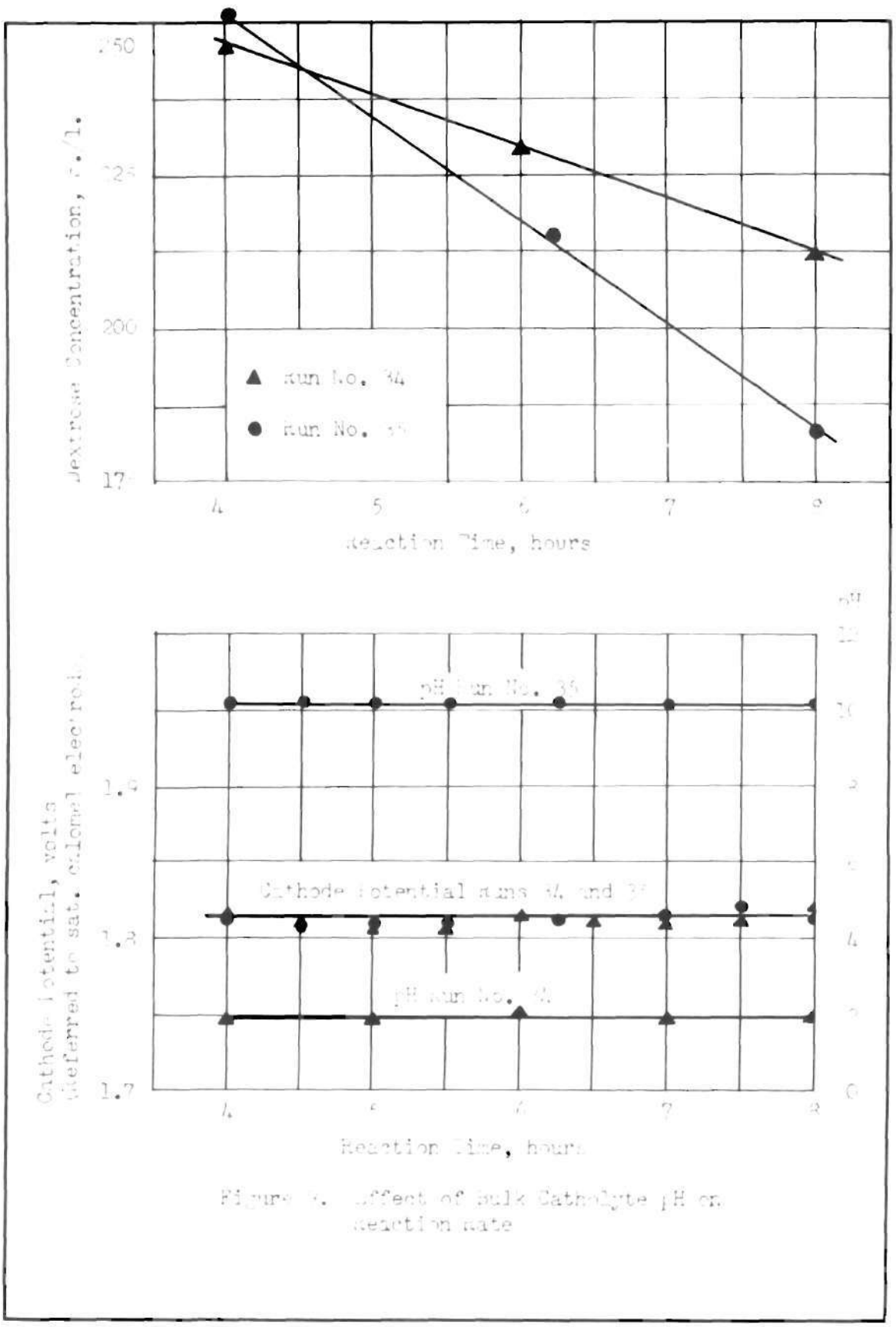


Figure 4. Effect of Bulk Catholyte pH on Reaction Rate

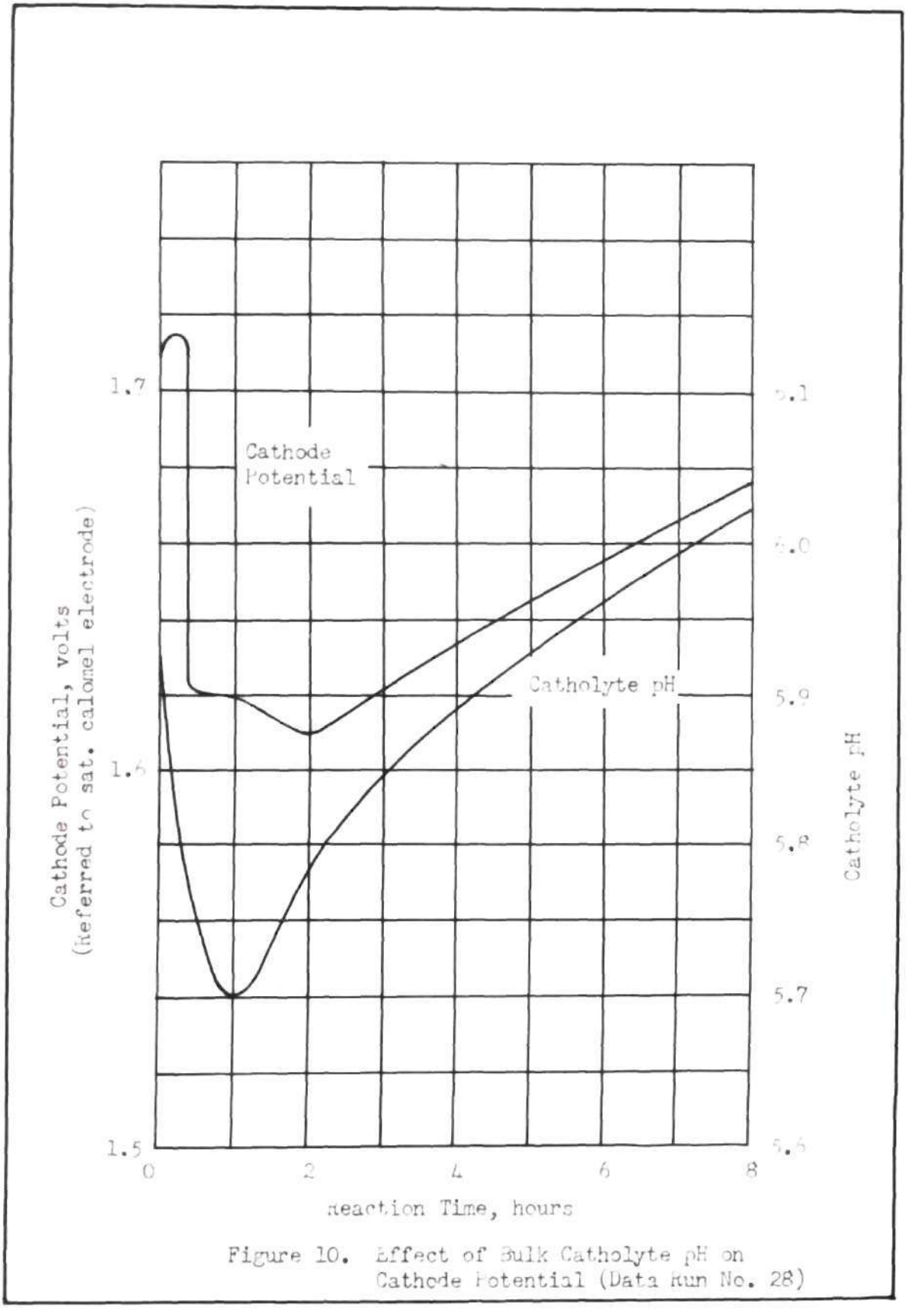


Figure 10. Effect of Bulk Catholyte pH on Cathode Potential (Data Run No. 28)

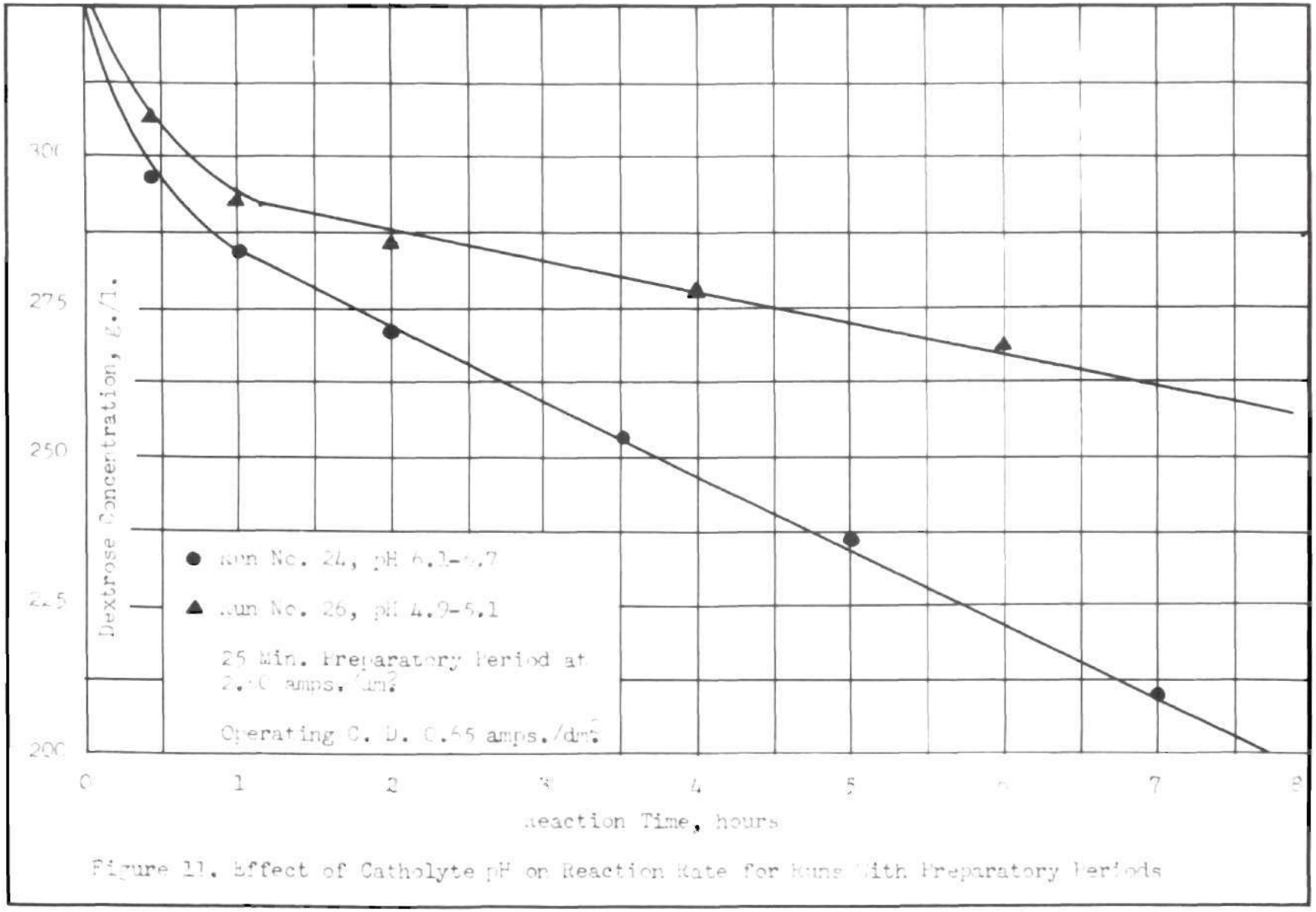


Figure 11. Effect of Catholyte pH on Reaction Rate for Runs With Preparatory Periods

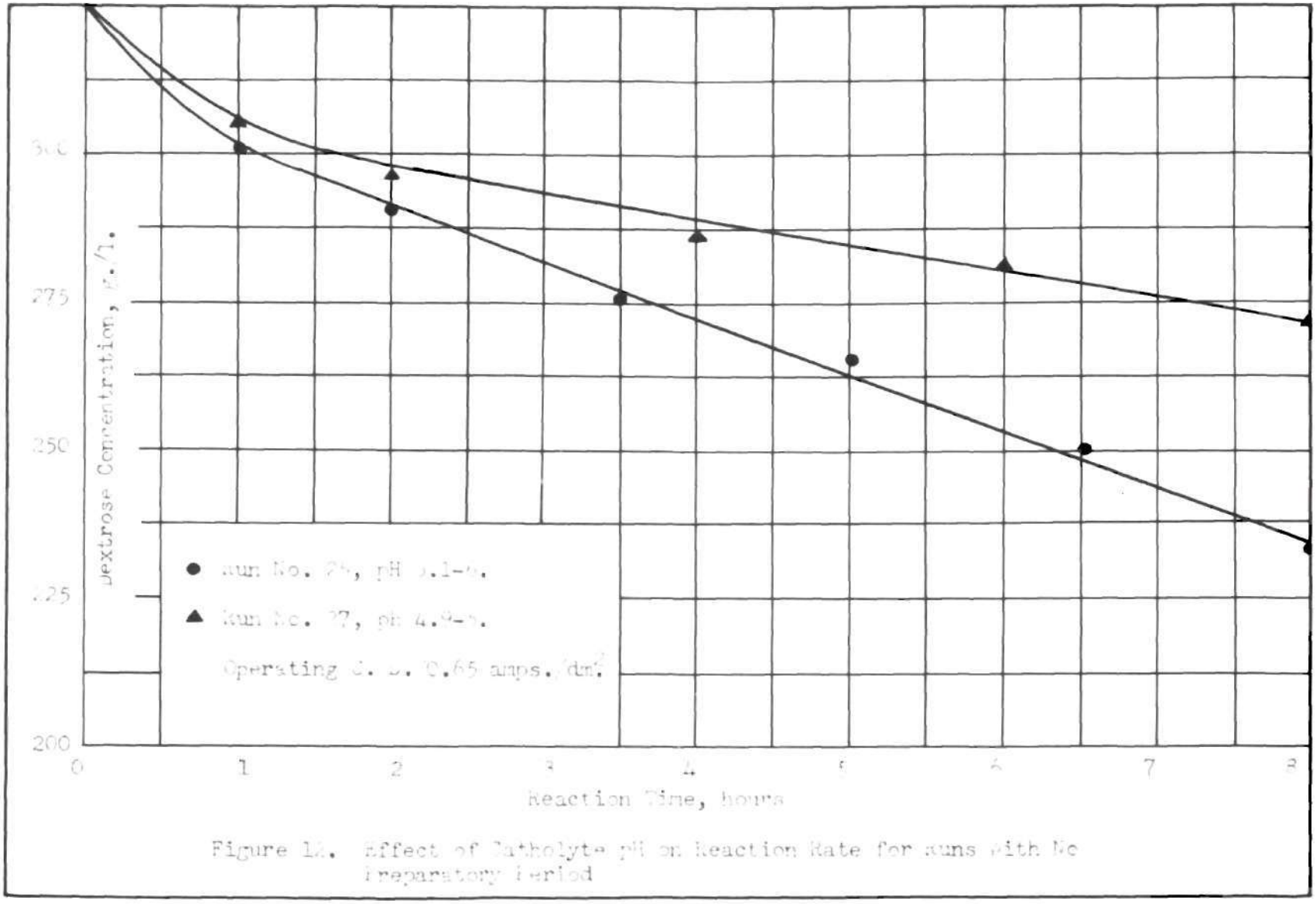


Figure 13. Effect of Catholyte pH on Reaction Rate for Runs with No Preparatory Period

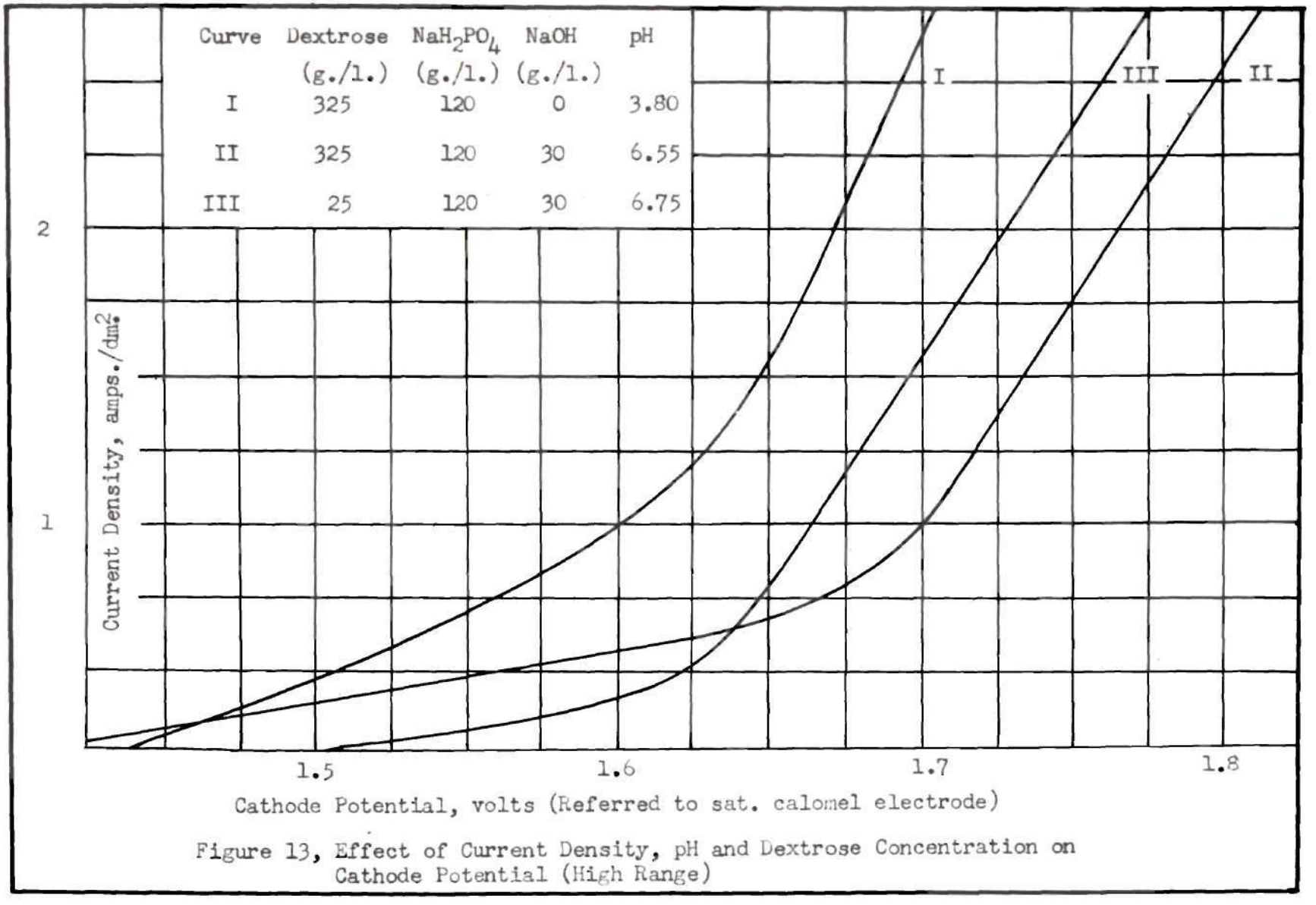


Figure 13, Effect of Current Density, pH and Dextrose Concentration on Cathode Potential (High Range)

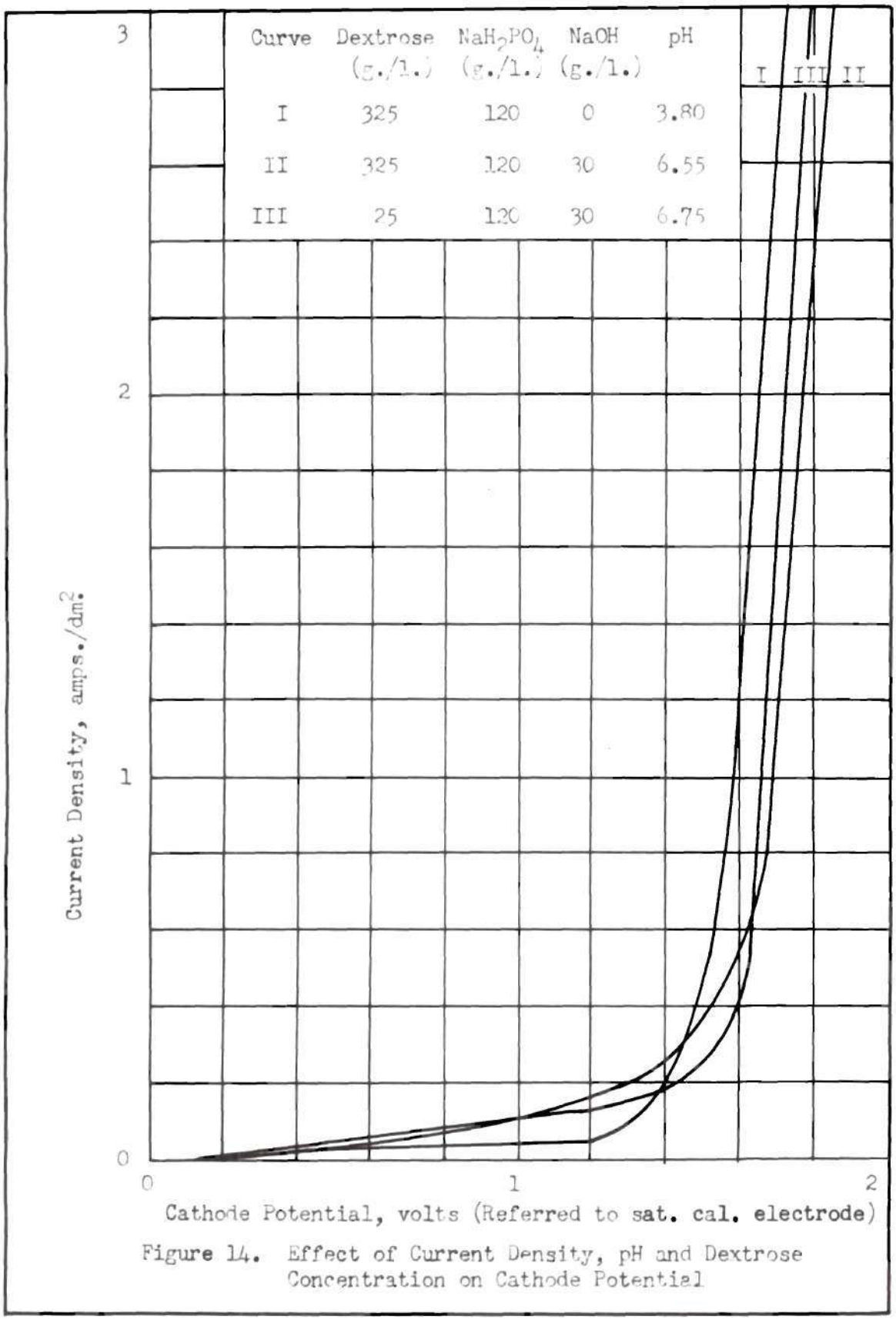


Figure 14. Effect of Current Density, pH and Dextrose Concentration on Cathode Potential

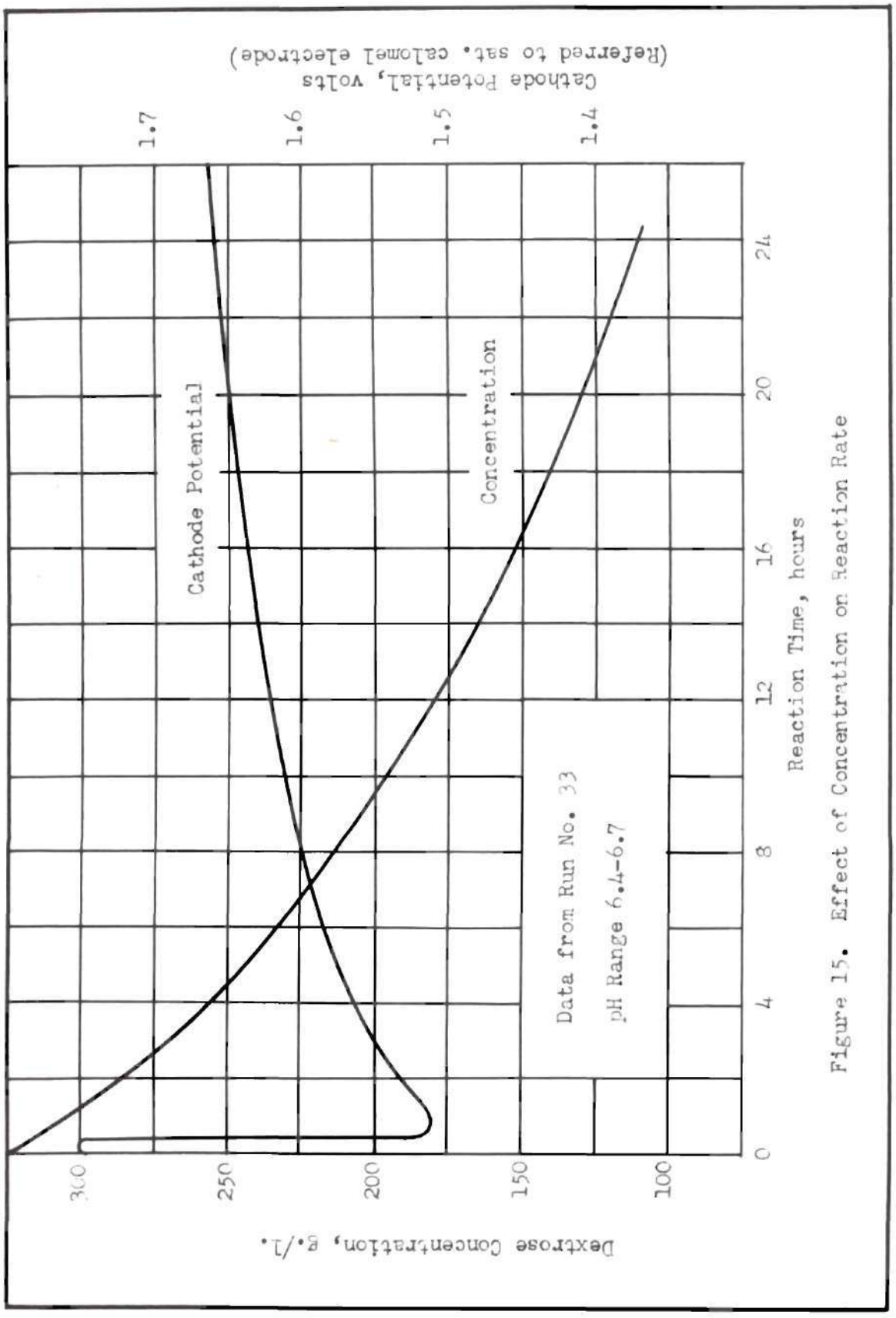


Figure 15. Effect of Concentration on Reaction Rate

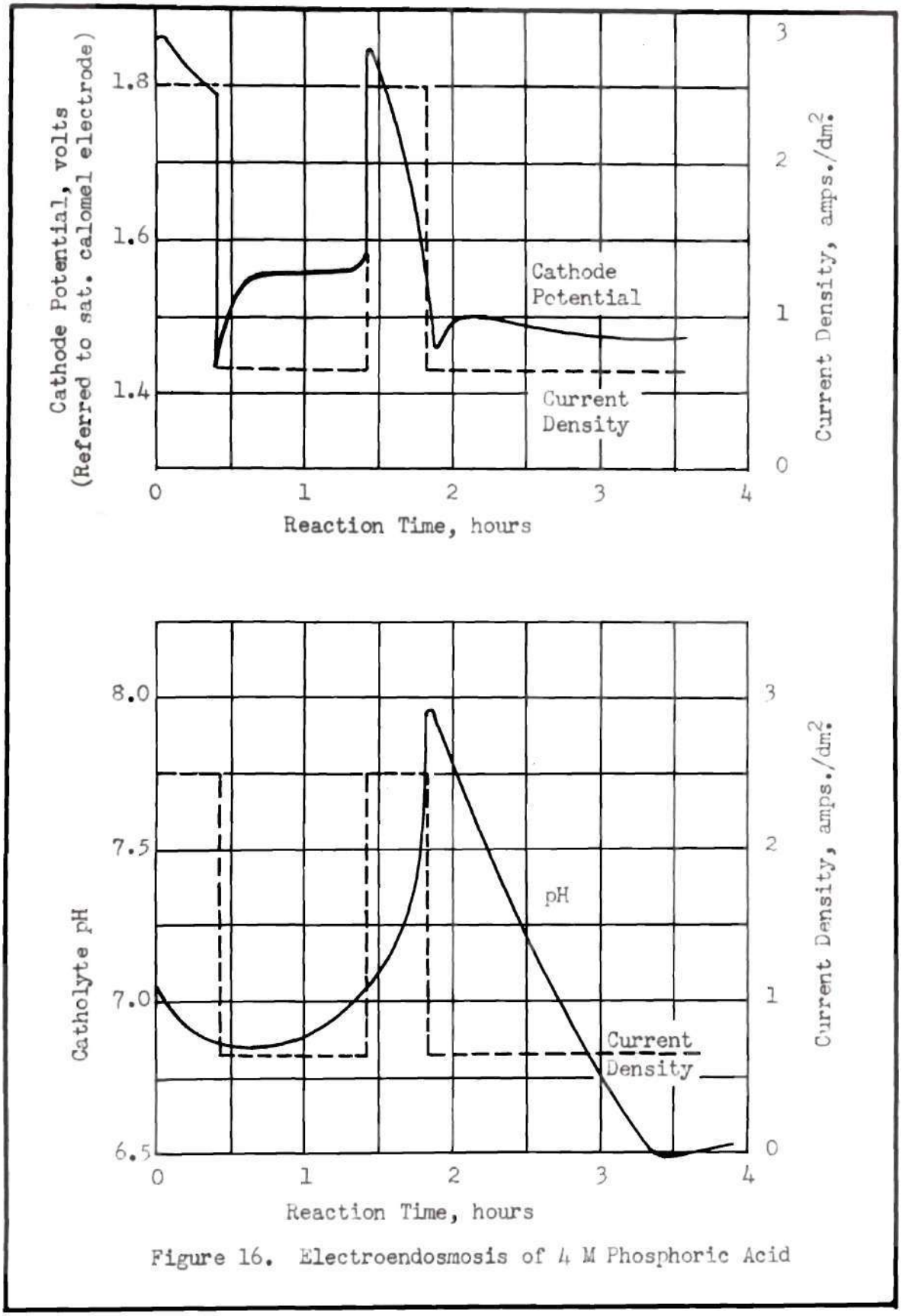


Figure 16. Electroendosmosis of 4 M Phosphoric Acid

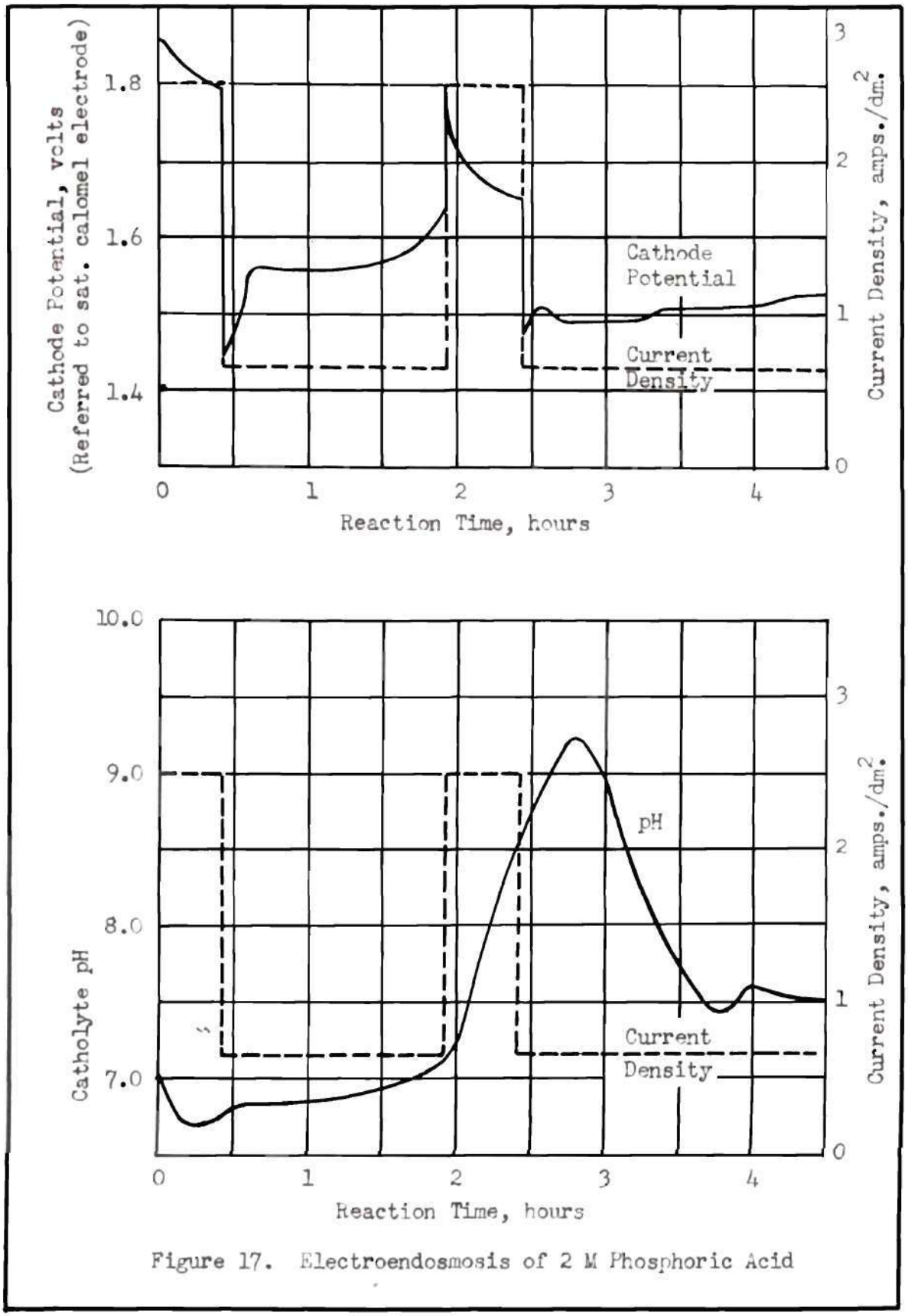


Figure 17. Electroendosmosis of 2 M Phosphoric Acid

DISCUSSION OF RESULTS

Reliability of Experimental Data

Accuracy of analytical methods.--Before examining the results obtained during the course of the experimental program, it is well to consider the accuracy of the various methods used to obtain these data. A large portion of the data was obtained by applying standard procedures for the quantitative determination of dextrose, sorbitol and carbon. The selection of these methods and their probable accuracy are discussed in detail in the section entitled "Analytical Methods". The estimated accuracy is repeated here for convenience.

Dextrose determination.....$\pm$ 1 %

Sorbitol determination.....$\pm$ 3 %

Carbon determination.....$\pm$ 3 %

The measurements of cathode potential, catholyte pH and current flow are dependent upon the precision of the electrical instruments used, and in the first two cases mentioned, upon the sampling techniques employed. These considerations were discussed in the section dealing with analytical methods. It was concluded that the error involved in these measurements is small.

Carbon balances.--During the course of the reduction reaction, there is continual diffusion of carbon containing compounds from the catholyte to the anolyte. A knowledge of the extent of this carbon loss is obviously important and is furnished in the present case by overall carbon balances

on the cell at the end of the run. Carbon balance data are available for runs 22 through 35 (Table 1). Inspection of the overall carbon balances indicates a range of recoveries from 97.5 to 102 per cent. These results are well within the estimated accuracy of the carbon determination method.

Reproducibility of results.—The reproducibility of the data may be established by reference to Figure 5 where the reduction rates of two runs made under substantially the same conditions are compared. The figure is a graphical presentation of the data of runs 7 and 8 (Tables 22 and 23). Actually, the catholyte was subjected to agitation in run No. 8, but as will be mentioned later, this had no effect on the rate of reduction. The reproducibility is evidently good. As will be shown later, this reproducibility is rather remarkable in view of all of the factors affecting the progress of the reaction.

Comparison of experimental results with existing data.—The preceding discussion indicates that the experimental data may be expected to be quite reliable and reproducible. A further indication of the validity of the data is furnished by comparison with available literature data. This criterion may be utilized in three cases. Runs No. 34, 33 and 35 utilized an unbuffered acid catholyte, a buffered acid catholyte and an alkaline catholyte, respectively, and were designed to provide a comparison with results obtained under similar conditions by other investigators. These comparisons will be presented in the order mentioned.

There are a limited amount of data in the literature concerning the electrolytic reduction of dextrose in an unbuffered acid catholyte.

The results presented by Hales (36) are typical of these data. In one case, using a current density of one amp./dm^2 and a catholyte containing 325 grams of dextrose per liter, 75 grams of sodium sulfate per liter and 0.5 to 1.5 grams of sulfuric acid per liter, 90 per cent of the initial dextrose had disappeared after 68 hours of operating time. The pH of the catholyte during this time interval was about 2.7 and the current efficiency was calculated to be about 42 per cent, based upon the disappearance of dextrose.

Under essentially the same conditions as those mentioned above, with the exception of the cathode material used, a current efficiency of 40.4 per cent was obtained in the experimental cell after 33.4 per cent of the initial sugar had disappeared. Since Hales does not present data for points intermediate between the start of the reaction and the point at which 90 per cent of the sugar has disappeared, no closer comparison can be made. However, the same author in another paper (24) states that for this system the reaction proceeds at a constant rate until rather low concentrations are reached. Thus, a comparison of current efficiencies during the constant rate periods of the two runs will give a fair appraisal of the operation of the cells. This is essentially what has been done above, since the constant rate period extends to about 30 or 40 grams per liter of dextrose in the catholyte. In other words, until this concentration range is reached the rate of reaction is constant and therefore not dependent upon the dextrose concentration. Somewhere in this range the rate of reduction becomes proportional to the dextrose concentration.

The conclusion to be drawn from the foregoing discussion is that

the data obtained for run 34 are compatible with those available in the literature for a run under substantially the same conditions.

As outlined in the introductory section entitled "Experimental Program", the modifications of the electrolytic reduction process suggested by Emerson (15) were investigated for one particular system, namely, a catholyte containing a sodium hydrogen phosphate - sodium hydroxide buffer and a cell utilizing a mercury-treated nickel cathode. Data for one run under these conditions and six runs under slightly different conditions are presented in the patent. These results are reproduced from the patent in Table 46 of APPENDIX II. Current efficiencies calculated from these data are quite different from those reported in the patent. A comparison of the calculated and reported results is afforded by Table 2 and a sample calculation is given in APPENDIX III.

Aside from the discrepancies noted above, it is interesting to compare results from the experimental cell with data from the patent. Except for a difference in the ratio of cathode area to catholyte volume, run 33 was carried out under exactly the same conditions as run 5 of the patent. After 24 hours of operating time the dextrose disappearance per equivalent of current and the current efficiencies tabulated below were obtained.

Run No.	Current efficiency (%)	Dextrose disappearance (gm.)
5	38.3	34.35
33	41.6	35.70

Run 35 was performed under conditions typical of those used in the commercial electrolytic process. An alkaline catholyte containing 325 grams of dextrose per liter, 75 grams of sodium sulfate per liter and no base or acid was reacted at a mercury-treated nickel cathode. The pH was allowed to rise to 10 and the entire run was conducted at a pH in the range 10 to 10.3. A current efficiency of about 48 per cent was obtained for the constant rate period between two and eight hours. In a similar run, using an amalgamated zinc cathode, Sanders and Hales (24) obtained a current efficiency of about 54 per cent during the constant rate period. The slightly higher efficiency of the commercial process could easily be due to the difference in the electrode material used.

The comparisons made in the three cases indicate favorable agreement with literature data under widely differing conditions. The results of other investigators can be substantiated using the equipment, techniques and analytical methods employed in this study. The results obtained from the experimental work may thus be directly compared with data available in the literature to evaluate the performance of the modified electrolytic process.

Summarized Data

Before discussing the results of the experimental work it may be well to restate the modifications of the electrolytic process which were studied.

The experiments were carried out with a buffered acid catholyte,

in contrast to the alkaline catholyte of the commercial process. The buffer system was sodium hydrogen phosphate-sodium hydroxide and the range of catholyte pH studied was from 4.5 to 7.0.

A mercury-treated nickel electrode was employed in contrast to the amalgamated lead or zinc cathodes used in industrial practice.

The operating temperature was generally about 120°F. In the alkaline catholyte used industrially, the temperature is maintained at about 70°F.

An anolyte of phosphoric acid was used rather than the conventional sulfuric acid anolyte.

The ceramic diaphragm of mullite had a permeability of about 1.65×10^{-6} darcys.

Positive steps were taken to insure an alkaline electrode film as suggested by Emerson (15) and electroendosmosis of bulk anolyte acid was investigated as a pH control mechanism.

General conclusions regarding the performance of the modified electrolytic process are difficult to formulate from the tabulated experimental data. However, certain tables constructed from these data present an overall picture of the results obtained and provide information for evaluation of the process. Thus, it is important, for purposes of evaluation, to know the current efficiencies, rates of reaction and degree of conversion to the desired products which can be expected under various operating conditions. The tabulated information discussed in this section is intended to fill this need.

Conversion of dextrose to sorbitol.--Since the formation of sorbitol is

the desired reaction in the electrolytic reduction of dextrose, as carried out in the buffered acid catholyte, it is interesting to know the fraction of the dextrose which disappears during a run that has been converted to sorbitol. This information is furnished for runs 22 to 35 by Table 3. It is quite clear that between 35 and 60 per cent of the disappeared dextrose does not go into the formation of sorbitol. Some of the dextrose unaccounted for as sorbitol shows up in the anolyte due to diffusion through the diaphragm and is consequently lost from the reaction zone. Since the diffusion rate was approximately constant in all cases (See Table 1), the data as presented are comparable. Some of the dextrose undoubtedly is converted to products other than sorbitol. The alkaline catholyte seems to facilitate a higher degree of conversion to sorbitol than does the buffered acid catholyte. The unbuffered acid catholyte has the same effect as the alkaline catholyte but to a lesser extent, although the most favorable results obtained with buffered solutions are about as good as those realized in the unbuffered acid electrolyte.

There are no data in the literature on dextrose conversion with which to compare these results.

Rate of reaction.--Table 4 shows the per cent reduction, i.e., the per cent of original dextrose disappeared, at the completion of various runs conducted with different current densities. A wide range of reduction rates is obvious and suggests the possibility of other factors being of equal importance to the current density itself. For an eight hour period, the greatest reduction was obtained using an alkaline catholyte,

but the results for run 24 using a buffered acid catholyte approach this result rather closely. Since approximately the same quantity of dextrose was present initially in each run, comparison of per cent reduction is a valid procedure.

Current efficiency.--The rate of reduction and the current efficiency during the reduction are naturally desired to be as great as possible. However, economic considerations determine the final choice of operating conditions and a lower reduction rate, with consequent decrease in unit capacity, will sometimes be selected to keep the current efficiency at a reasonable value. In Table 5 current efficiencies and per cent reduction, as previously defined, are presented for runs 7 to 35. The current efficiencies range from 20 to 67 per cent. Current efficiencies for data available in the literature range from about 15 per cent to 55 per cent (52,25,26).

Comparison of catholytes.--Table 6 shows the rate of dextrose disappearance at a current density of one amp./dm^2 (a value used frequently in industrial practice) for three basically different catholytes. Better results were obtained in the two unbuffered solutions than in the buffered catholyte. The alkaline catholyte produced results which were quite superior to those obtained in the other two solutions.

The effect of time.—The variation of dextrose concentration during a long run is presented in Table 7 (Figure 15) and the effect of buffer salt concentration is given in Table 8.

The tables prepared for this section were intended to furnish the reader with a general view of the experimental results. It may

be concluded, from this rather superficial examination of the data, that the modified electrolytic process compares favorably under certain conditions with the results obtained in the commercial electrolytic process. The relative desirability of the two procedures and an understanding of the factors affecting the modified process will require a more thorough study of the data. The following sections of this discussion will deal in detail with rate of reaction, dextrose conversion, current efficiency and electroendosmosis.

Rate of Reduction

The inherently slow rate of dextrose reduction in the electrolytic cell has already been mentioned as one of the prime reasons for the conversion of commercial production facilities to the high pressure catalytic process. Consequently, any modifications of the electrolytic process designed to place it in a competitive position with the newer process must either result in increased reduction rates, or some other feature which makes it much more desirable than the older commercial electrolytic process.

The modifications suggested by Emerson (15) have been studied to determine what, if any, improvement could be expected in the rate of reaction. As indicated in the discussion of the summarized data, the performance of the electrolytic cell in this respect was about the same as the commercial cell using an alkaline catholyte. The data gathered during the experimental program, however, were of such a character that several conclusions can be drawn concerning the

factors affecting the reduction rate. The following sections will consider the influence of the variables studied.

Alkaline cathode film.--As outlined in the Introduction, it has generally been conceded that an alkaline environment facilitates the reduction of dextrose. Whether this is due to the reduction of the enediol form present in the alkaline solution as suggested by Cake (53) or the increased susceptibility of the carbonyl group to reduction in alkaline media (29) is uncertain. At any rate, dextrose is more readily reduced in alkaline solution and one would expect difficulty with electrolytic reduction in acid solution.

That the electrolytic reduction does proceed in an acid solution is explained by the existence of an alkaline cathode film which forms spontaneously as current is passed through the cell. The existence of this film is an actuality which may be established by simple tests in certain cases. Thus, in run 34, carried out at a pH of 1.5 to 2, it was possible to extract from the cathode surface minute samples which had pH values of about 11, as indicated by pH test paper. This run was made with a catholyte containing sodium sulfate and sulfuric acid according to the conditions specified by Hales (25).

With the modifications suggested by Emerson (15), it was more difficult to detect the alkaline film by sample removal. Such samples were usually mildly acid or weakly alkaline. It is probable that the buffer salt in the catholyte makes it more difficult to establish a pH gradient and consequently hinders formation of a highly alkaline film.

Several other qualitative observations indicate the existence of alkaline conditions at the cathode. A liquid pH indicator applied

to the exposed tabs of the cathode and allowed to flow down into the catholyte will indicate the presence of such a film. Phenolphthalein indicator was used successfully in this manner in many cases. It was also found, in general, that the pH of a well mixed catholyte, at the immediate completion of a run, was higher than that of the bulk catholyte. This could be due to a zone of high alkalinity on the electrode surface. When the surface of a cathode, which had been removed from an operating cell and allowed to drain, was washed with distilled water, the pH was found to be 7.05. The pH of the water itself was 6.4.

These qualitative observations, especially the first mentioned, confirm the existence of the alkaline film. The actual mechanism of film formation may be rather complicated, but a simple process may be envisioned. Current flowing through the electrolytic cell is carried proportionately by all of the ionic species depending upon their concentration and mobility. However, for each equivalent of current passed through the cell, one equivalent of ions is discharged at each electrode. In the case under consideration, the only cations present in the catholyte are hydrogen and sodium ions. The net result is that one equivalent of hydrogen is liberated for each equivalent of current passed. Since only a fraction of this amount of hydrogen migrates to the cathode under the influence of the electric current, there is a depletion of hydrogen ions from the area surrounding the cathode and the pH of this film consequently tends to become alkaline. This alkaline region does not extend too far into the body of catholyte because of the increased diffusion of hydrogen ions caused by the concentration gradient so established. At some point the concentration gradient (and likewise the pH gradient) will reach

such a magnitude that the sum of the hydrogen ions brought to the cathode by diffusion and electrical transport will just equal the hydrogen ions discharged. At this point the film will become reasonably stable.

If there is a buffer salt in the catholyte it will function to offset the depletion in hydrogen ions at the cathode surface, and the film formed, if any, will also be dependent upon the diffusion of fresh buffer salt to the electrode. The higher the rate of this diffusion the more difficult will be the establishment of an alkaline film. Thus, the buffer salt in the catholyte would be expected to hinder the formation of an alkaline film. That this expectation is realized is illustrated by the difficulty experienced in getting an alkaline sample from the cathode when a buffered acid catholyte is used. This subject will be considered further when the cathode potential is discussed.

It was previously noted that only sodium and hydrogen ions are present in the electrolytes to migrate toward the cathode and it was stated that the net result of the passage of one equivalent of current was the liberation of one equivalent of hydrogen. It is well to consider what happens to the sodium ions in the solution.

Normally, with a plain metal cathode, sodium ions can not be discharged because of the high negative electrode potential required. In the case of a mercury surface with its high hydrogen overvoltage, however, it is possible for sodium ions to be discharged and form a sodium amalgam on the cathode surface (54). Actual sodium amalgam formation was detected in run 35. In this experiment the cathode was carefully removed immediately after the completion of the run. Ridges of pasty amalgam were observed on the cathode surface, reacting with the water

still clinging to the electrode. Some of this material was scraped into a small container of distilled water and continued to react with the water for some time. At the completion of the hydrogen evolution the water gave an alkaline reaction and a small pool of mercury remained in the container.

A quantitative picture of the alkaline film has not been obtained and the reaction will consequently have to be considered in the light of other observations.

While discussing the alkaline film it is appropriate to consider the value of the steps taken to cause its rapid formation at the start of the reaction. Emerson (15) suggests two procedures designed to accomplish this purpose. The first, which consists of direct application of liquid alkali to the cathode surface, was attempted only once. The results of this test were unsatisfactory in that no noticeable change in reaction rate was observed until the catholyte was quite near the basic range. The pH got out of hand into the basic range and the run (No. 13) was discarded. The true merits of the method are therefore undetermined but it is obvious that the technique of alkali application will require some development.

The second suggested procedure, which is relatively simple to utilize, is that of subjecting the cell to an abnormally high current density at the start of a run to build up the alkaline film rapidly. In almost all of the experiments where this procedure was followed, a current density of 2.5 amps./dm^2 was used.

The effect of the high current density preparatory period on the reduction rate is clearly illustrated in Figures 6 and 7. Figure 6

is a graphical presentation of the data of runs 23, 24 and 25 in which high current density preparatory periods of 5 minutes, 25 minutes and 0 minutes respectively were used. These runs all started with a catholyte pH of 6.55. Figure 7 is derived from the data of runs 26 and 27 (Tables 36 and 37). In this case a preliminary high current density period of 25 minutes was used for run 26. No preparatory period was used in run 27. These experiments were carried out at a starting pH of 4.95.

Inspection of Figure 6 indicates that the reaction rate is increased appreciably by the high current density preparatory period. Not only does the reduction occur at a more rapid rate during the preparatory period, but the subsequent reaction occurs at a greater rate. As will be seen later, some of this increase in rate is undoubtedly due to the increase in bulk catholyte pH which occurs during the high current density period.

In the case of catholytes at a lower starting pH, the effect is not quite so pronounced. In fact, the rates of reduction of the two cases in Figure 7 appear to be about the same after the initial high rate during the preparatory period of run 26. Apparently, the pH gradient which can be developed at this lower catholyte pH is rather small because of the buffer action of the electrolyte, and the larger gradient built up by the preparatory treatment can not be maintained.

An appreciable amount of space has been devoted to the discussion of the alkaline film. Very little mention has been found in the literature concerning this subject except the indication of its presence in several cases. This is probably due to the difficulty involved in

the study of this phenomenon. In the present paper the film has not been studied directly, but rather through its effect on the reaction rate as discussed above.

The factors to be considered subsequently can probably be illustrated more satisfactorily than the alkaline film but are in much the same situation because of their complex interrelation. What appears to be one of the most important of these variables is the cathode potential.

Cathode potential.--Regardless of the theory of electrode potential which one accepts to explain the experimental facts, it is clear that the rate of reduction should be increased by an increase in cathode potential. This conclusion was reached in the introductory discussion of cathode potential after consideration of some of the proposed theories. The data of Table 9 bear out this conclusion. These results are presented graphically in Figure 8. The data of runs 22 to 30 were examined to determine the average rate of reaction for periods during which the cathode potential remained constant or varied only slightly. The catholyte pH during all of these runs was in the range between 4.5 and 7. The rate of reaction as it is used here was calculated from the dextrose disappearance after a correction had been made for the dextrose lost by diffusion. A sample calculation illustrating the procedure used to obtain these data is given in APPENDIX III.

Where several products can be formed, the desired one can sometimes be obtained in high yield by control of the cathode potential. Thus a given cathode may possess varying degrees of reducing ability with a given depolarizer, depending upon the cathode potential maintained.

As an example of this situation, consider the case of the reduction of nitrobenzene (55). At a cathode potential of -1.0 volt, the reduction product is mainly hydrazobenzene. However, at -0.6 volts azoxybenzene, a less highly reduced substance, is formed in quantity. This indicates that a more vigorous reduction will occur with a given depolarizer at higher cathode potential.

With all of the possible products obtainable by the electrolytic reduction of dextrose it is evident that control of the electrode potential might be the key to control of the distribution of the possible compounds in the final product. In this case, however, the situation is complicated by the extensive transformations which occur in the alkaline film. The products are by nature complex and defy the ingenuity of the organic chemist even to identify them. Their quantitative determination would certainly be difficult. It should be possible, however, to investigate the effect of potential on sorbitol and mannitol formation.

The data collected during the experimental program show a trend toward increased conversion of dextrose to sorbitol with decreasing current density. This is illustrated in Table 10, where the per cent of dextrose actually reacted, i.e., exclusive of that lost by diffusion, is tabulated for runs 22 to 35. The effect of cathode potential and catholyte pH on the degree of conversion is less obvious. For each run the range of both potential and pH is indicated, but it is impossible to state the true average during a given run. Since the true average value of each variable can not be determined, it is difficult to draw conclusions which are even qualitative in nature.

Table 10 also shows that quite a spread in the degree of dextrose conversion is possible at one current density. At 0.65 amps./$dm.^2$, for example, the conversion decreases roughly as the chronological order of the runs. The lower conversions are most likely due to the combined effects of the pH and cathode potential prevailing during these runs, as will be mentioned later when the conversion of dextrose to sorbitol is considered.

At a current density of one amp./$dm.^2$ the unbuffered alkaline and acid catholytes facilitated higher degrees of conversion than the buffered acid solution of run 28. However, it is possible to obtain as good or better conversions with buffered acid catholytes at somewhat lower current densities (Runs 29 and 22).

In summarizing the effect of electrode potential on the rate of electrolytic reduction, it is proper to conclude that under given conditions increasing the cathode potential will increase the rate of reaction. Consideration of the factors which affect the electrode potential itself will be deferred until the effects of these variables on the rate of reaction are discussed.

pH of bulk catholyte.--The effect of the pH of the main body of the catholyte on the rate of reduction may be nicely illustrated by runs 34 and 35. In these runs no buffer salt was used in the catholyte. Conductivity was supplied in each case by 75 grams per liter of sodium sulfate. In run 34 the catholyte was maintained at a pH of 1.7 to 2.3 while the pH in run 35 was held between 10.0 and 10.3. The results are compared graphically in Figure 9.

Reference to the figure indicates that the cathode potential prevailing in each case was the same. However, the reaction rate in the alkaline catholyte of run 35 was substantially greater than that in the unbuffered acid catholyte of run 34. Only the last four hours of the two experiments are compared because control of the acid pH was not satisfactorily established until this point.

In each of the two cases under consideration a constant high electrode potential was obtained and in the unbuffered acid catholyte of run 34 a very easily detected alkaline film was present. The difference in reaction rate is attributed to the effect of the difference in catholyte alkalinity. The observed effect may be explained by the fact that in the alkaline catholyte the dextrose has already undergone the Lobry de Bruyn-Van Ekenstein transformation to such an extent that the concentrations of the various transformation products do not vary much from their equilibrium concentrations at the pH prevailing at the cathode surface. As the various resultants of the transformation are reduced their concentrations change to maintain this equilibrium. In acid solution, on the other hand, the sugar in the body of the catholyte is far from the equilibrium which prevails in the cathode film on the surface of the electrode. In diffusing through the alkaline film toward the cathode the sugar molecules undergo the transformation to some extent depending upon the retention time in the film. Thus, if it is the intermediate enolic form which is actually reduced, as supposed by Cake (53), the lower rate of reaction in the acid solution could be explained by a slow rate for the enolization reaction.

In the alkaline catholyte, the sugar has already undergone the

transformation and the concentration of forms which are being reduced is such that the reaction occurs at a constant rate until very low dextrose concentrations are reached. In the acid solution, as will be seen later, the rate of reduction falls off with decreasing concentration. This indicates the possibility that in alkaline solution the concentration of the reducible forms is such that, until low dextrose concentrations are reached, only the electrode potential governs the rate of the reaction, while in acid solutions the concentration of reducible forms is low enough in the alkaline film to be a controlling factor along with the cathode potential, even at relatively high dextrose concentrations in the catholyte.

It is interesting to note that in the presence of a stable, easily detected alkaline film developed at the cathode in run 34, the same cathode potential was obtained as that in the alkaline electrolyte of run 35. With a buffer salt present in the catholyte, however, the cathode potential is markedly affected by the pH of the body of the solution. This is illustrated in Figure 10 which is derived from the data of run 28 (Table 38). The increase of electrode potential with catholyte pH is a phenomenon common to all of the runs in buffered solution and would be evident from plots of any of the experimental data.

As will be mentioned later, the cathode potential that can be obtained at a given current density rises with the pH of the solution. The dependence of cathode potential on catholyte pH indicates that it is very difficult to maintain an appreciable pH gradient in the solution. This is to be expected in view of the strong buffering action of the

sodium hydrogen phosphate-sodium hydroxide system. The feature of the process that is so effective as a pH control mechanism is likewise effective in preventing or seriously hampering the development of an alkaline environment at the cathode.

The effectiveness of the sodium hydrogen phosphate-sodium hydroxide buffer system is illustrated in Figure 31 (APPENDIX I), which is a graphical presentation of the data recorded in Table 19 (APPENDIX I) (56). The solutions for which these data apply contained 325 grams per liter of dextrose.

The effect of pH in the buffered acid catholyte is evident from the data of runs 24 and 26, or 25 and 27 which were made at high and low pH respectively in each of the two groups. Runs 24 and 26 utilized 25 minute preparatory periods; runs 25 and 27 used no preparatory periods. These data are presented in Figures 11 and 12.

The effect of the pH of the bulk catholyte on the cathode potential obtainable at a given current density is illustrated by Figure 13 derived from the data of Table 20 (APPENDIX I). Curves I and II were obtained at pH values of 3.80 and 6.55 respectively. This covers fairly well the range of alkalinity prevailing in the buffered acid catholytes used in the experimental work. It will be noted that in the buffered solution a relatively small decrease in pH has an appreciable effect on the cathode potential. This is in contrast to the unbuffered acid catholyte of run 34 where a cathode potential equal to that in alkaline solution was obtained. It is reasonable to conclude that at a given current density, the electrode potential is a measure of the alkalinity

of the film surrounding the cathode. This conclusion is compatible with equation (1) discussed in the Introduction, which indicates that a decrease in hydrogen ion concentration, i.e., an increase in pH, results in an increase in the cathode potential.

Dextrose concentration.--It has already been stated that previous investigators have found the reduction rate of dextrose in alkaline solution to be constant until very low concentrations are reached (24). That this is not the case in the buffered acid catholyte employed in the modified electrolytic process is illustrated by the data of run 33. These data are presented graphically in Figure 15. This conclusion is even more apparent from the results reported in Table 11. This table was obtained by determining the average rate of dextrose disappearance for three hour intervals during the run and recording the appropriate average concentrations during these intervals.

If the results of Table 11 are plotted it will be noted that the average rate of dextrose disappearance is almost linear with average concentration, and practically proportional to it, in spite of steadily rising cathode potential. The rising cathode potential would be expected to offset the effect of decreasing concentration to some extent, but a conclusion to this effect can not be based on the experimental data.

Since the pH of the catholyte remained in a very narrow range and the electrode potential increased as the reaction proceeded, the only obvious reason for a decrease in reaction rate with time is the effect of decreasing dextrose concentration. If the surface of the cathode became roughened during the reaction, the cathode potential would be

expected to decrease because of the decrease in current density, i.e., the surface roughening amounts to an increase in cathode area and a consequent decrease in current density. From the data presented here it would seem that in a buffered acid catholyte the dextrose concentration effects the reaction rate at much higher concentrations than it does in basic solution. A possible explanation of this fact has already been discussed in the section dealing with the effect of bulk catholyte pH on reaction rate. It was postulated that a slow stage in the enolization transformation would tend to cause the concentration of reducible compounds in the alkaline film to be appreciably lower than the equilibrium concentrations at the pH of the film. The decreasing dextrose concentration would tend to decrease the concentration of the reducible forms to an even greater extent.

It is apparent then that the rate of reduction is affected by the dextrose concentration when a buffered acid catholyte is used. Since the experimental data are limited and the effects of the individual variables can not be definitely isolated, it is difficult to draw quantitative conclusions concerning the concentration effect. However, from the limited data available, it appears that the rate of reduction is proportional to the dextrose concentration.

The dextrose concentration also affects the cathode potential that can be obtained at a given current density. The extent of this effect is illustrated by Figure 13, which was derived from the data of Table 20 (APPENDIX I), as already mentioned. Comparing curves II and III of Figure 13 note that appreciable decrease in dextrose concentration has a noticeable effect on the electrode potential at a given current

density. Since the static potentials in the two solutions vary because of the different composition, the curves cross at a low current density. The full range of data for these current density-cathode potential curves is plotted in Figure 14.

The similarity between the shape of these curves and that for a poor depolarizer (curve III) presented in Figure 1 of the Introduction is evident.

Current density.--The effect of current density has already been discussed in a general way in connection with the summarized data of Table 4. It is very difficult to hold all of the variables constant to study the effect of current density on the reaction rate. It is obvious that high current density is accompanied by a high rate of hydrogen discharge, but the fraction of this liberated hydrogen which is efficiently utilized is dependent on many other factors. Thus, the pH, temperature, electrode material, surface characteristics, etc., would certainly be expected to exert an influence on the process occurring at the cathode. An attempt has been made to eliminate certain of these variables by keeping them constant in all runs, but there is a limit to which this procedure can be followed. The obvious effect of current density is the influence it has on the cathode potential that may be obtained under a given set of conditions. Referring again to Figure 13, the variation of cathode potential with current density for three different catholyte systems appears to occur exponentially. In view of this relationship, a decrease in current efficiency as the current density is increased beyond a certain point would be expected. In other words, large increases in

current density result in a relatively small increase in cathode potential at high current densities. It is possible, of course, that this slight increase in potential is just what is required to cause a certain reaction to occur. In this case an increase in efficiency is conceivable.

One may conclude from the foregoing discussion that current density is an important factor in so far as it affects the cathode potential which can be obtained under given conditions. The effect of current density itself on the rate of reaction in buffered acid solution is difficult to describe quantitatively because of the concurrent effect of other variables.

Other variables.--So far the effect of cathode potential, catholyte pH, dextrose concentration and current density on the rate of electrolytic reduction has been considered. There are numerous other variables which might conceivably affect the reaction, but it is impractical to examine each of them in a reasonable period of time. Thus, operating temperature, electrode material, electrode surface characteristics, diaphragm permeability, diaphragm material, ratio of cathode area to catholyte volume and a host of other less important factors have not been studied. These variables are rather easy to hold constant from run to run and this procedure was resorted to in all cases. Certain other variables were explored briefly and will be discussed along with the anticipated effect of those which were not studied.

One might expect that in a process which involves diffusion of reactants to the cathode, as does the electrolytic reduction of dextrose,

the rate of reaction should be increased by agitation of the solution. However, in the case of dextrose reduction with a buffered catholyte, diffusion was found not to be the rate determining process. Thus run 8, previously described, duplicated the conditions of run 7 with the exception that the catholyte was agitated in the former case. Figure 5 indicates the lack of effect due to agitation. Presumably, the alkaline film in a buffered solution is not affected by moderate agitation because the film is extremely thin and adheres rather strongly to the surface of the electrolyte.

The agitation was supplied in the above case by the device shown in Figure 23 of the section entitled "Equipment". The agitation blade made approximately six strokes per minute.

The effect of buffer salt concentration was discussed previously. Reference to Table 8 indicated that a two fold increase in concentration resulted in only a slight increase in reduction rate. However, this increase was probably due to the higher catholyte pH prevailing in the case of the more concentrated solution. From previous discussion it is evident that the buffer salt hinders alkaline film formation and therefore an increase in its concentration would be expected to cause no change or to cause poorer results.

The effect of temperature, which was not studied, is rather difficult to predict. Hales (25) states that in unbuffered acid solution an increase in temperature does not appreciably change the rate of reaction from that at 70°F. It is not certain that this conclusion can be made in the case of buffered catholytes. The experiments carried out with such solutions utilized operating temperatures of about 120°F.

This is about the upper limit permissible with the diaphragm used. It is not known what effect higher temperatures would have on the stability of the dextrose. The effect of a lower operating temperature is pure speculation. The lower temperature would slow the rate of reaction and the diffusion rate through the alkaline film. It would make the film more viscous and possibly thicker because of the lower rate of diffusion of the buffer salt toward the electrode. Thus, experimental investigation would be required to determine the exact influence of operating temperature.

The electrode material for alkaline solutions has already been investigated by Swann (23). If an alkaline cathode film is assumed in acid solution, the same conclusions should apply. The effect in the buffered acid solution would be expected to be about the same; namely, high hydrogen overvoltage metals, such as mercury, should produce good results. This point would also have to be studied from an experimental standpoint.

Surface characteristics of the cathode have certain predictable effects on the reduction rate. Because of the consequent lower current density caused by roughening of the surface, lower cathode potentials can be predicted. Increased current efficiency usually accompanies this roughening effect. Roughening of the electrode surface, just mentioned, sometimes occurs during the course of an electrolytic process. The effect of crystal structure, previous history, etc., of the electrode is also a matter for further study.

Diaphragm permeability is important because of its effect on diffusion of catholyte materials into the anolyte. Electroendosmosis

should be independent of permeability but will be affected by the nature of the diaphragm material, i.e., by the sign and magnitude of charges on the surface of the diaphragm pores. The diaphragm material is likewise important from the standpoint of resistance to electrolyte solutions and the contaminants which might be introduced into the catholyte. Thus, as previously stated, small amounts of magnesium, even as low as one part per million of total solids, cause a marked decrease in reaction rate (26).

The ratio of cathode area to catholyte volume at a given current density defines also the current concentration, i.e., the current per unit volume of catholyte. Glasstone reports that Tafel has found that an increase in current concentration increases the current efficiency, at constant current density, for a relatively slow reaction (57).

High current concentration is said to favor rapid side reactions. The obvious value of high current concentration is the decreased retention time of the reducible material and products in the catholyte when there is danger of decomposition.

It is evident that many factors affect the rate of the electrolytic reduction of dextrose in a buffered acid catholyte. The effect of these variables is summarized in the following section.

Summary-rate of reduction.--The electrolytic reduction of dextrose proceeds more rapidly in alkaline than in acid media. However, it is possible, even in acid solution, to carry out the reduction at a reasonable rate, by virtue of the alkaline film which forms spontaneously on the cathode. Such a film is desirable, but its formation is greatly hindered by the presence of a buffer salt in the catholyte. Special

steps taken to insure the formation of an alkaline film in a buffered acid catholyte are more advantageous at high than at low pH.

The cathode potential governs the rate of reaction to a great extent, higher potentials making for higher rates. Higher potentials are obtainable at pH values nearer the high end of the acid range than at lower pH. Cathode potential increases with current density under a given set of conditions, according to a power relationship. Both pH and dextrose concentration affect the potential obtainable at a given current density.

The reaction rate in a buffered acid catholyte is affected adversely by decreasing dextrose concentration. This is in contrast to the results obtained in alkaline solution where the rate is independent of concentration until low concentrations are reached.

The lower rates generally obtained in a buffered acid catholyte than in an unbuffered solution are due to the lower electrode potentials obtainable and the difficulty experienced in developing an appreciable pH gradient.

Since the high pH of the film is necessary both for the enolic transformation to occur and for the development of high electrode potentials, the main difficulty experienced with the modified process may be laid directly to the action of the buffer salt. At high pH in the acid range, the deleterious effect of the buffer is less pronounced.

Neither agitation nor increase in buffer salt concentration cause an increase in the rate of reduction. The effect of temperature and nature of the electrode surface have not been investigated and

their influence is difficult to predict.

End Products of the Reaction

The optimum stability of dextrose is reached at a pH in the interval between 3 and 4 according to Kröner and Kothe (58). If reduction of dextrose could be carried out in this range of pH it is reasonable to assume that very little degradation would occur and a rather pure product should result. In the electrolytic process, however, there is spontaneous formation of an alkaline cathode film so that the dextrose is subject to degradation and transformation while in this film. Because of the many reducible forms present in the film, and the possibility of degradation in the alkaline solution, somewhat less than 100 per cent of the reduced sugar would be expected to show up as sorbitol. The following discussion is intended not only to indicate the degree of conversion of dextrose to sorbitol, but also to show the extent of sugar loss by diffusion into the anolyte. This information is necessary to evaluate the process for the production of sorbitol.

Conversion of dextrose to sorbitol.--Some of the possible reduction products of dextrose which have actually been identified in the catholyte of an electrolytic cell under alkaline conditions were mentioned in the Introduction. It is reasonable to assume that reduction in acid solution would produce much the same array of compounds, since in reality the reduction takes place in an alkaline atmosphere at the electrode surface. The study of the reduction products is not within the scope of the present work. However, by means of chromatographic adsorption

analysis it is possible to isolate a sorbitol zone and subsequently to determine the sorbitol content of the sample placed on the column. This procedure, which has been discussed under the heading "Analytical Methods", was used to determine the sorbitol contents of the catholytes of runs 22 - 35.

There are no data in the literature with which to compare the sorbitol determinations, but the information obtained with the alkaline catholyte of run 35 and the unbuffered acid catholyte of run 34 can be used for comparison purposes. It has already been shown that data for these runs are compatible with literature data with respect to per cent reduction and current efficiency.

Reference to Table 10 indicates approximately the same degree of conversion of dextrose to sorbitol for the two runs mentioned. Values for runs in the buffered acid catholyte vary on either side of those for the runs using unbuffered catholytes. At 0.65 amps./dm^2 there are data for seven runs under varying conditions of pH and electrode potential. As mentioned previously, it is not possible to state true average values of these variables and the evaluation of their effect on the degree of conversion of dextrose to sorbitol is consequently rather difficult. Reference to the table does indicate, however, that combination of a low pH range and a low cathode potential range makes for lower conversions at a given current density. Lack of knowledge of the true average operating pH and cathode potential makes it impossible to draw anything but such a rough qualitative conclusion.

From the data presented in Table 10, it is evident that as good as or better degrees of conversion can be obtained in the buffered

acid solution as in the unbuffered solutions. However, somewhat lower current densities must be employed to reach comparable degrees of conversion. This limitation has a serious impact on the utility of the process, since it results in lower capacity for each reduction cell unit.

In referring to Table 3 previously, the statement was made that the unbuffered catholytes led to higher degrees of dextrose conversion to sorbitol. It is evident that two different bases have been used for consideration. In the case discussed previously, when considering the summarized data, the actual fraction of original dextrose which disappeared and was converted to recoverable sorbitol was considered. In the present case the per cent of recoverable material represented by sorbitol is under consideration. The actual conversion to sorbitol is undoubtedly higher than the data indicate because any sorbitol which has diffused can not be detected.

Each of the bases used to express the conversion of dextrose to sorbitol is useful. Basing the conversion on the dextrose originally present provides a means of evaluating the efficiency of the process for sorbitol production. Using the recoverable organic material in the catholyte as a basis provides information necessary for the design of separation and purification procedures. In the ideal case the two bases would result in the same conclusion since there would be no loss by diffusion.

As mentioned previously there are no comparable conversion data in the literature. Thus, Emerson (15) considered neither the products of the reduction nor the loss of dextrose by diffusion, but concentrated

attention on the apparent reduction as indicated by the total disappearance of dextrose. Other investigators, considering alkaline and unbuffered acid catholytes, have reported sorbitol content as the semi-empirical pyridine number. It appears that sorbitol has the ability to form a crystalline complex with pyridine which is insoluble in cold pyridine. Only 2-desoxysorbitol forms a similar compound. Therefore, it is possible to devise a test in which the weight of dry sorbitol recovered from a given weight catholyte sample, through the intermediate formation of this sorbitol-pyridine complex, can be used as a relative index of the sorbitol content of the sample. This method was investigated and found to be tedious and time consuming with the additional disadvantage that, at best, only a relative indication of sorbitol was obtained. The chromatographic procedure is simpler and provides absolute data on the sorbitol content of a sample.

Diffusion through diaphragm.--As mentioned previously, a certain fraction of the dextrose disappearing during the course of any one run is lost by diffusion from the catholyte to the anolyte. For an eight hour period this diffusional loss amounted to between 4.77 and 7.57 per cent of the original carbon present in the catholyte. Thus, the diffusion amounted to about 6 per cent of the carbon initially in the catholyte. The exact proportion of each diffusing compound is not known but what is important is that this material represents a loss in efficiency. As mentioned previously, the diaphragm used had a permeability of about 1.7×10^{-6} darcys in contrast to 5×10^{-5} darcys recommended by Emerson (15). Thus, it seems that an even lower permeability is necessary to reduce the

loss by diffusion to a reasonable figure.

That this diffusion is not due to electrokinetic effects in the diaphragm is illustrated by the fact that under operating conditions, but with no current flowing, 9 per cent of the original carbon was found in the anolyte after 8.42 hours. This seems to indicate that during the flow of current, there is a slight electroendosmosis or flow of anolyte liquor through the pores into the catholyte which actually tends to hinder the diffusion to some extent.

There are no literature data available as to the extent of diffusion experienced in the practice of the commercial process or obtained by other investigators. Undoubtedly, this difficulty has been taken into consideration industrially because of the economic aspects involved. Here again, one must balance the cost of sugar lost by diffusion against the increased cost of power when a less permeable diaphragm is used and the electrical resistance of the cell is increased.

Summary-end products of the reaction.--In summarizing the material concerning the end products of the reduction, a comparison with results of other investigators can not be made, but the following conclusions can be formulated.

The electrolytic process for the reduction of dextrose in a buffered acid catholyte, of the type considered here, results in the conversion of from about 33 to 64 per cent of the original dextrose to recoverable sorbitol, depending upon the conditions employed. From 47 to 84 per cent of the organic material in the catholyte, exclusive of dextrose, was sorbitol. As previously mentioned, current density

has a noticeable effect on the degree of conversion of dextrose to sorbitol. The influence of pH and cathode potential is not as evident.

In considering the fraction of initial sugar converted to sorbitol it appears that generally higher conversions are obtained in the unbuffered catholytes.

In eight hours of operating time about 6 per cent of the initial sugar is lost by diffusion into the anolyte. The distribution of compounds which are lost by this process is not known.

Current Efficiency

The efficient utilization of electrical energy is naturally of great importance in any electrolytic process. With a poor depolarizer such as dextrose in the catholyte it is impossible to obtain reasonable rates of reduction at 100 per cent current efficiency. Hydrogen gas was evolved from the buffered acid catholyte, used in the experiments reported here, at current densities as low as 0.05 amps./dm^2 This value is much too low to be used in a commercial installation. Thus, current efficiencies somewhat less than ideal are to be expected at reasonable current densities. The exact range in which these efficiencies fall must be determined from experimental data.

Definition of current efficiencies.--Current efficiency may be defined on any basis one desires. As mentioned previously, many investigators report efficiencies in terms of the ratio of original reactant which has disappeared over a given time interval to that which should react theoretically if the current were 100 per cent effective. Where there is loss of reactant by any process other than electrolytic reduction or

oxidation this efficiency is obviously meaningless. Thus, in the present case the loss of dextrose by diffusion is included in the total disappearance of dextrose and current efficiencies calculated from the disappearance of the sugar are misleading. Up to this point all current efficiencies have been reported on this basis to facilitate comparison with literature data.

For purposes of discussion, three current efficiencies will be defined. The efficiency based upon total dextrose disappearance, as mentioned above, will be termed the "apparent current efficiency". The "actual current efficiency" is then the value calculated by taking into consideration the fact that part of the total dextrose disappearance is due to a permanent loss by diffusion. The "sorbitol efficiency" will be defined in terms of the ratio of recoverable sorbitol in the catholyte to that which should be produced theoretically, assuming that only sorbitol is produced from the original sugar.

Comparison of efficiencies.--Table 12 presents the three efficiencies defined above for runs 22 - 35. Since carbon balance data and sorbitol determinations are not available for previous runs they are not included in the table. All of the runs were approximately eight hours long, except for run 33, which was terminated after 24 hours and is consequently omitted from the table.

At a current density of 0.65 amps./dm^2 it is evident from the table that the pH of the buffered catholyte has a definite effect on the sorbitol efficiency. Thus, the sorbitol efficiencies range from high to low in exactly the same order as the bulk catholyte pH. The sorbitol

efficiency at 0.45 amps./dm.^{2} is lower than that obtained at 0.65 amps./dm.^{2} in the same pH range. This is probably due to the effect of the lower cathode potential obtained at the lower current density. At higher current densities the sorbitol efficiency is also lower than it is at 0.65 amps./dm.^{2} In the case of run 28 at 1.00 amps./dm.^{2} the lower efficiency may be due to a rather low operating pH, but in run 30 at 1.25 amps./dm.^{2} the pH and electrode potential were reasonably high. It is interesting to note in this case that under conditions of pH and electrode potential roughly the same as run 24, the sorbitol efficiency is only one half of what it is in run 24 where about one half of the current density was employed. Some consideration will reveal that the absolute amount of sorbitol formed in the two cases during the operating time is about the same. This further illustrates the prime importance of catholyte pH and cathode potential, and the secondary importance of current density when considering the rate of reduction of dextrose in a buffered solution, i.e., it is the cathode potential resulting from a given current density which is of more importance than the current density itself.

The comparison of the three different catholytes, namely, unbuffered acid, buffered acid and alkaline catholytes, may be made by referring to runs 34, 28 and 35 respectively.

The results obtained in an alkaline catholyte were superior to those in either of the two other solutions, while the data for the unbuffered acid catholyte are better than those for the buffered solution. The conclusion to be drawn from these data is that both a high electrode potential and an alkaline atmosphere facilitate the attainment of

high sorbitol efficiencies. The effect of these variables on the degree of conversion of dextrose to sorbitol is less evident.

The tabulated efficiencies indicate that it is possible to obtain results in the buffered acid solution comparable to those in alkaline solution, but that a somewhat lower current density must be employed. This, of course, implies immediately that the rate of reduction will be somewhat lower in the buffered solution.

Summary-current efficiency.--Three different current efficiencies can be defined for purposes of discussion of the experimental data. Since sorbitol is the main product of the reduction, a good deal of consideration has been given to the so-called "sorbitol efficiency". The "apparent efficiency", which is reported by most investigators, has been calculated to facilitate comparison with literature data.

Both a high cathode potential and an alkaline environment appear necessary for the attainment of high sorbitol efficiencies. Efficiencies comparable with those obtained in alkaline solution are realizable in the buffered acid catholyte at a somewhat lower current density.

Electroendosmosis

The importance of catholyte pH is quite evident from preceding sections of this discussion. The importance of pH control prompted Emerson (15) to suggest the use of a buffer salt in the catholyte. By employing the appropriate buffer system it should be possible to conduct the reduction within the confines of a very narrow range of pH and thus control the quality of the resulting product. The sodium hydrogen

phosphate-sodium hydroxide buffer system results in a pH range intermediate between the alkaline and the rather low pH catholytes previously investigated. The buffered catholyte makes pH control a minor problem, but a tendency toward increasing the pH still exists and must be counteracted by the addition of acid to the catholyte. In the overall process as much acid must be added as when using an unbuffered catholyte.

There are two methods to be considered for the addition of acid to the catholyte. The obvious one is that of direct addition to the catholyte. The second and more novel is the addition of acid by electroendosmosis of the anolyte acid. Electroendosmosis is the bulk movement of the anolyte liquid through the pores of the diaphragm under the influence of the electric potential gradient. Little need be said about the method of direct acid addition except that it has the disadvantage of localized high acid concentration and the possibility of disturbing an alkaline film if present. Electroendosmosis, on the other hand, presents the advantage of uniform acid distribution at a rate dependent upon the current strength employed.

The feasibility of using electroendosmosis as a pH control mechanism in conjunction with the buffered acid catholyte was investigated. The following discussion concerns the results obtained in this investigation.

Data from the reduction cell.--Runs 31 and 32 were designed to determine the effect of high current density on the electroendosmosis of 4 and 2 molar phosphoric acid respectively. In each of these two experiments a high preparatory current density period of 0.42 hours at 2.50 amps./$dm.^2$

was used. At 0.42 hours the current density was decreased to 0.65 amps./$dm.^2$ and was maintained at this value until the bulk catholyte pH reached about 7.05. At this point the current density was again raised and maintained at 2.50 amps./$dm.^2$ for 0.42 hours in the case of the 4 molar acid (run 31) and 0.50 hours in the case of the two molar acid (run 32). At the end of the high current density periods the current density was again reduced to 0.65 amps./$dm.^2$ The pH and electrode potential were recorded periodically during the runs.

Referring first to Figure 16, which is a graphical presentation of the data of run 31, it appears that electroendosmosis of the 4 molar anolyte acid does actually occur during the period of high current density. There is an appreciable lag in the response of the system to the acid added to the catholyte by this mechanism since the acid must diffuse from the wall of the diaphragm to the body of the solution. In this particular case, about 0.087 additional equivalents of current were required to decrease the pH of 300 ml. of solution from 7.05 to 6.5. It would normally take about two hours and fifty minutes, at the current density employed, to pass this much current through the cell. Thus, for even a small addition of acid by this method an appreciable expenditure of electrical energy is required.

Further complication is introduced by the effect of the high current density on the electrode potential. At the initiation of the high current density period, the cathode potential rises to a high value, but then proceeds to drop off. When the high current density period is discontinued the potential drops to a low value and never returns to the value prevailing before changing the current flow. This lowering of

the cathode potential is probably due to the effect of the lower catholyte pH. However, this explanation is not satisfactory for the observed effect while the catholyte pH is in the alkaline range. It is possible that the high current density period causes a roughening of the electrode surface, but there are no experimental data to substantiate this view.

In Figure 17 the data of run 32 with 2 molar phosphoric acid anolyte are presented. Essentially the same results were obtained in this case, as in the previous one, with the exception that the catholyte pH was never brought back down into the acid range.

The electroendosmosis of anolyte acid in this particular case does not seem feasible. However, using a larger ratio of cathode area to catholyte volume would increase the effectiveness of the method because, as will be seen later, the flow due to electroendosmosis is dependent on the total current. With a smaller catholyte volume and the same current density, the same amount of acid will be moved electroendosmotically, but a larger pH change will occur in the catholyte. Thus, Emerson (15) was apparently able to use electroendosmosis to control the pH in the runs reported in his patent because the ratio of cathode area to catholyte volume employed was 15.4 $dm.^2$/liter compared to 10.0 used in the experimental work reported here.

Although electroendosmosis may be used as a pH control mechanism when high ratios of cathode area to catholyte volume are employed, its practicality is somewhat questionable. The expenditure of energy required is large for the result obtained and complications arise because of the disturbing effect on the cathode potential. The electroendosmosis of anolyte acid appears to be more a matter of academic interest than

industrial importance. Direct addition of acid to the catholyte through properly placed distribution tubes would appear to be much more economical and easily controlled.

The amount of phosphoric acid anolyte which must be added to a given volume of catholyte to reduce the pH to the desired value may be simply determined by reference to the curves of Figure 32 (APPENDIX I), plotted from the data of Table 21 (APPENDIX I). The data from which these curves were derived were obtained in solutions containing 325 grams per liter of dextrose. It was found that the addition of dextrose to made a solution of this concentration changed the pH of a 2 molar buffer solution from 6.81 to 6.49. Thus, the dextrose itself has an appreciable effect on the pH of the solution, which must be taken into account.

The electroendosmosis of phosphoric acid through a porous diaphragm has been studied by Bruns (59) for several concentrations of acid and several current densities. Since these data bear directly on the problem at hand and have not been published they will be presented briefly here.

Data from electroendosmotic cell.--The electroendosmotic cell used by Bruns (59) is illustrated in Figure 33. The data obtained are tabulated in Tables 47 - 50. Figures 34 and 35 were derived from these data. These figures and tables are located in APPENDIX II. The diaphragm used in these experiments was of the same material used in the diaphragm of the electrolytic cell. The material is "mullite", a compound of aluminum oxide and silicon dioxide. As explained in the section entitled "Equipment", the permeability of this material is about 1.7×10^{-6} darcys

and the pore diameter was found to be about 3.8 microns. The porosity, i.e., void fraction, is about 35 per cent.

The theoretically derived equation for electroendosmosis may be stated as follows: (60)

$$V = \frac{D\ I\ Z}{4\pi n\ k(300^2)} \qquad (4)$$

where V is the volume rate of flow through the pores of the diaphragm in cc./second, D is the dielectric constant in $(e.s.u.)^2/dyne\ cm.^2$, I is the current flow in amperes, Z is the Zeta potential in volts, n is the viscosity in poises, k is the specific electric conductance in the pores of the diaphragm in ohm cm.

A discussion of the Zeta potential and the derivation of this equation is beyond the scope of the present discussion. It suffices to say that the Zeta potential represents a potential developed at the interface of the solid and liquid phases in the diaphragm, which is responsible for the observed electrokinetic effect, i.e., electroendosmosis. The subject of electrokinetic effects is discussed in most physical chemistry texts and an especially comprehensive treatment by Abramson (61) is available. Adam (62) presents an excellent discussion in connection with electrical phenomena at interfaces.

Figure 34, derived from the data of Table 48 (APPENDIX II), shows the effect of current strength on the volume of acid transported per second by electroendosmosis with molarity of the acid as a parameter. From these same data, and known data for the dielectric constant, the viscosity and the electrical conductivity, Bruns calculated values of

the Zeta potential. These values were compatible with data in the literature for similar substances, and are reported in Table 48 (APPENDIX II).

In Figure 35 the milimoles of acid transported per second is plotted as a function of molarity with current strength as a parameter. These data indicate that mole rate of flow of acid is independent of the molarity. From equation (4) it is evident that at a given molarity, the flow is determined by the current strength, I. Therefore, if the data of Figure 35 are extrapolated to 2 or 4 molar acid and equation (4) is used to extrapolate the data to higher current strengths, an approximation of the flow to be expected due to electroendosmosis in the electrolytic cell can be obtained. Thus, at 7.5 amperes (2.5 amps./dm.^{2}), as used in runs 31 and 32, the flow of 2 molar anolyte acid would be predicted as follows: at 1.0 amperes, the mole rate of flow is constant with molarity and is equal to about 5×10^{-3} milimoles per second. Dividing by the molarity, the volume rate of flow is

$$\frac{5.2 \times 10^{-6}}{2} = 2.5 \times 10^{-6} \text{ liters/sec. or } 2.5 \times 10^{-3} \text{ cc./sec.}$$

At 7.5 amperes the volume rate of flow would then be

$$\frac{7.5}{1} (2.5 \times 10^{-3}) = 18.75 \times 10^{-3} \text{ cc./sec.}$$

and the mole rate of flow would be

$$(18.75 \times 10^{-3} \text{ cc./sec.})(2 \times 10^{-3} \text{ moles/cc.}) = 37.50 \times 10^{-6} \text{moles/sec.}$$

or 37.5×10^{-3} milimoles/sec. For a period of 30 minutes this flow would

be 67.5×10^{-3} moles of 2 molar H_3PO_4. From Figure 32 it is estimated that this much acid should alter the pH of 300 ml. of catholyte containing 1 molar sodium hydrogen phosphate buffer from 7.05 down to about 6.7.

From Bruns's data the predicted effect of the high current density period of run 32 would be to lower the catholyte pH from 7.5 to 6.7 in the absence of any other pH controlling effects. However, the high current density causes a rapid depletion of hydrogen ions from the solution, which must also be compensated. The exact extent of the depletion is difficult to determine by analytical treatment because of the lack of information concerning the activities of the ions in the solutions. This information is necessary to calculate the fraction of current carried by the hydrogen ions, and in turn the depletion of hydrogen ions in the catholyte.

It is safe to conclude that the possibility of pH control by electroendosmosis of anolyte acid exists. That there is actually a measurable transport of phosphoric acid by this mechanism is proved by the data of Bruns. The extent of the transport is rather limited, however, and the method would probably be usable only with systems using high ratios of cathode area to catholyte volume and very high current densities. On the other hand, under some conditions the depletion of hydrogen ions might overbalance the effect of the acid added and the pH would actually rise.

From consideration of the theoretical equation (4), it is obvious that the rate of flow by electroendosmosis is proportional to

the total current flow. Likewise, the discharge of hydrogen ions is proportional to the current flow. Therefore, if the current is raised to cause an increase in electroendosmosis, an increase in hydrogen ion discharge will also occur. If there is an increase in catholyte pH during a period of normal current flow, it is due to depletion of hydrogen ions from the catholyte at a rate greater than hydrogen ions can be added to the catholyte by means of ionic transport, electroendosmosis and diffusion. When the current is increased, all of these quantities except diffusion increase in the same proportion so that, theoretically, it is impossible in this case to lower the cathode pH by inducing greater electroendosmosis. The results of run 31, which show such pH lowering effect, may be due to a difference in hydraulic head between the cathode and anode compartments, although an attempt was made to eliminate this possibility.

It is possible that difference in hydraulic head between the cathode and anode electrolytes might be a simpler and more effective means to obtain uniform distribution of acid added to the catholyte. In any case, the use of electroendosmosis as a pH control mechanism in industrial processes is rather impractical because of the economic considerations involved, if not because of the ineffectiveness of the technique itself.

Evaluation of the Modified Process

The data discussed in the preceding sections presents a rather complete picture of the features of the modified electrolytic process

proposed by Emerson (15). This section has as its main purpose the presentation of the relative merits and disadvantages of the particular modification studied.

Advantages.--The most interesting possibility suggested by the modification of Emerson (15) is the introduction of a buffer into the catholyte to control the pH. Since pH control is of much greater importance when alkaline solutions are used, buffered alkaline catholytes could be of even greater interest. The use of the NaH_2PO_4 - NaOH buffer in the present work made for very effective control of the catholyte pH.

The nickel electrode with a uniform mercury surface undoubtedly has the advantage of high mechanical strength compared to amalgamated lead or zinc electrodes. This feature is especially important if high operating temperatures are employed. Amalgamation of lead and zinc electrodes further weakens them internally while, in the case of nickel, the treatment occurs only on the surface.

With the buffered acid solution of dextrose, the end product of the reaction is always a water-white solution in contrast to dark-colored solutions obtained at high alkalinity. The sorbitol efficiencies which can be obtained with the modified process are as great as those resulting from the process in alkaline solution at somewhat higher current densities.

Disadvantages.--The buffer salt present in the catholyte, while presenting an effective means of pH control, likewise hinders the formation of an appreciable pH gradient at the cathode. Consequently, it is difficult

to develop a good alkaline environment at the cathode even in weakly acid solutions. The alkaline film has been shown to be a necessity when carrying out the reduction in acid solution, because of its effect on the cathode potential and the enolization of dextrose. The rates are generally lower in the buffered acid catholyte than in the alkaline or unbuffered acid solution.

The preliminary high current density period designed to insure an alkaline film has a measurable effect on the rate of reaction, but this is most likely due to the accompanying increase in pH rather than the establishment of a good film. The electroendosmosis of anolyte acid likewise occurs to a measurable extent, but the utility of this method as a pH control mechanism is doubtful. In any case, the cost of these procedures would probably outweigh the value of the results produced.

The relative operating costs of the two processes from a standpoint of the materials involved is summarized in Table 13. It is apparent from this rough comparison that from a raw materials standpoint the modified process is much more expensive than the standard commercial process. According to the table, there is almost a two-fold increase in cost based on these data. This conclusion may be somewhat misleading if recovery and reuse of the chemicals is practiced, but laboratory experience indicates that the removal of the phosphate buffer salt from the catholyte entails certain difficulties which would have to be eliminated. The lower rates to be expected would also make for a more expensive process, since the capital outlay to obtain a given production capacity would be greater. The separation of the inorganic constituents of the catholyte from the organic material represents a certain fraction

of the cost of the overall process. The relative costs of the separation procedures would have to be investigated for the two processes under consideration.

The nickel electrodes recommended would likewise entail a higher initial investment, but might pay dividends in longer utility.

A ceramic diaphragm of the permeability suggested, i.e., 5×10^{-5} darcys, is not satisfactory if loss of sugar by diffusion is to be kept to a reasonable minimum. The higher electrical resistance of a less permeable diaphragm would increase the power loss to some extent. The increase in power cost must be balanced against the value of the decreased diffusional losses of dextrose.

From an economic standpoint it is possible to tolerate some loss of dextrose by diffusion rather than experience higher power consumption due to use of a less permeable diaphragm. Electric current is quite costly and therefore the amount of sorbitol produced per unit of current must be as high as possible. The fraction of reacted dextrose which goes to form sorbitol is important also because of the cost of separation and purification of the final products. Finally, the usable current density is quite important because it governs the capacity of the individual production units.

Summary.—The modifications suggested by Emerson (15) and studied during the course of the experimental program do not improve the electrolytic process for the reduction of dextrose to sorbitol. In addition to decided limitations of the various modifications, the process would probably be more costly to operate than the commercial process.

In view of the experimental evidence, it must be concluded that the modified electrolytic process can not be put on a competitive basis with the older commercial process and consequently can not be expected to compete with the process for the production of sorbitol by the high pressure catalytic hydrogenation of dextrose.

CONCLUSIONS

The conclusions which may be formulated as a result of the experimental investigation may be summarized as follows:

1. The data reported in this thesis are reliable, reproducible and compatible with data existing in the literature in cases where comparisons can be made.

2. The modified electrolytic process for the reduction of dextrose can not be considered to be competitive to the commercial electrolytic process and consequently can not be expected to compete with the catalytic process. No appreciable improvement in rates of reduction, current efficiency or sorbitol formation was observed during the course of the research program.

3. The rate of reduction is affected markedly by the cathode potential obtainable. Both catholyte pH and dextrose concentration affect the cathode potential, the former being the more important.

4. The electrode potential obtainable in an unbuffered acid catholyte does not seem to be affected by pH. On the other hand, the potential obtainable in a buffered solution is quite dependent upon the pH. A stable, easily detected alkaline film is formed spontaneously in an unbuffered catholyte, while it is more difficult to establish the actuality of such a film in a buffered solution.

5. The addition of a buffer to the catholyte, while providing an effective means of pH control, hinders the formation of a pH gradient or alkaline film at the cathode. The deleterious effect

of the buffer on the desired film is noticed even in catholytes which are only weakly acid. The best domain of operation for the process is at a pH near 7.0.

6. The rate of reaction is affected by the dextrose concentration in a buffered acid catholyte. This is not the case in an alkaline catholyte.

7. Neither agitation of the catholyte nor increase in buffer salt concentration produces noticeable effects on the progress of the reaction.

8. Using the buffered catholyte in the modified process, from 33 to 64 per cent of the disappeared dextrose was converted to recoverable sorbitol. Of the dextrose actually reacted, from 47 to 84 per cent was converted to sorbitol. There is a trend toward a higher degree of conversion with decreasing current density. Current efficiencies and degrees of conversion of dextrose equal to those obtained with the conventional electrolytic process can be realized with the modified process employing a buffered catholyte at somewhat lower current densities. In other words, the current can be as efficiently utilized to form sorbitol in the modified process as in the commercial process but the prevailing rate of reaction is somewhat less.

9. Sugar losses by diffusion through the porous diaphragm amounted to about 6 per cent of the original sugar during an eight hour run. Dextrose disappearance by this process seems to have been overlooked in the runs reported by Emerson (15).

10. The positive steps suggested to insure an alkaline film on

the cathode produce a measurable effect at pH values relatively high in the acid range. At a pH of about 5, no effect is detected.

11. Electroendosmosis of anolyte acid occurs to some extent, but the rate of addition of acid by this process is such that it is not an effective or economically feasible technique for industrial application.

12. The modified process would be more costly to operate than the conventional electrolytic process, because of the lower rate of reaction realized at equal current densities. Stated in another way, the modified process is less efficient at any given rate of reaction. The raw material costs are higher for the modified process, and the recovery and reuse of the chemicals might be more difficult than in the case of the commercial process. The use of electroendosmosis as a pH control mechanism and the high current density preparatory period would probably entail extra costs.

RECOMMENDATIONS

In view of the conclusions reached as a result of the research program herein described, further investigation of the modified process is not warranted, except as a matter of academic interest.

There are certain points which have not been resolved as a result of this study, which might be of interest. Thus, the use of a catalyst in the catholyte might be advantageous. Ions capable of existing in two stages of oxidation, such as cerium, iron, vanadium, titanium and chromium sometimes supply such catalytic action. The high valence form of the ions, such as Ti^{++++}, are reduced at the cathode to the lower valence stage (Ti^{+++}) in which form the ions are powerful reducing agents. The reduced form of the ion reacts with the depolarizer with the regeneration of the high valence form.

The use of a buffer for pH control in the catholyte of the process utilizing an alkaline solution might prove interesting. No increase in reaction rates over those prevailing in the commercial process are to be expected, but more accurate control of product quality should be facilitated. The addition of acid necessary to replace the hydrogen ions depleted as the reaction proceeds might be simply accomplished by maintaining a difference in liquid level between the anolyte and catholyte.

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APPENDIX I

Table 14. Effect of Firing Temperature on the Permeability and Porosity of Slip-cast Diaphragms*

Diaphragm No.	Firing Temperature (°F.)	Permeability (Darcys)	Porosity** (%)
3	1976	1.71×10^{-6}	11.6
8	1976	1.39×10^{-6}	9.63
4	2030	2.47×10^{-6}	14.5
6	2093	0.84×10^{-6}	6.43
5	2156	0	2.34
7	2156	0	2.50

*Casting slip consisted of the following:
30% Ball Clay
20% Kaolin
15% Talc
15% Feldspar
20% Flint

**Defined here as per cent of wet diaphragm weight due to adsorbed water, i.e., as per cent of weight of wet diaphragm due to adsorbed water.

Table 15. Analysis of Known Dextrose Samples Using Copper Reduction Method

Sample No.	Dextrose (mg./cc.)	NaH_2PO_4 (mg./cc.)	NaOH (mg./cc.)	Dextrose Found (mg./cc.)	Error (%)
1	1.625	0.600	0.150	1.630	0.31
2	1.625	0.600	0.150	1.625	0
3	1.625	0.600	0.150	1.650	1.54
4	1.625	0.600	0.150	1.650	1.54
5	1.625	0.600	0.025	1.635	0.62
6	1.625	0.600	0.025	1.635	0.62
7	1.625	0.600	0.100	1.645	1.23
8	1.625	0.600	0.150	1.630	0.31
9	1.625	0.600	0.100	1.645	1.23
10	1.625	0.600	0.150	1.635	0.62

Table 16. Comparison of Analytical Methods for the Determination of Dextrose

Sample No.	Composition	Analytical Method	Dextrose Found (mg./cc.)	Error (%)
1	2.2980 mg./cc. dextrose	Iodometric Oxidation	2.19* 2.27**	-4.7 -1.2
2	2.1140 mg./cc. dextrose 0.5 M H_3PO_4	Failed		
3	2.150 mg./cc. dextrose 0.5 M H_3PO_4	Copper Reduction	2.26 2.24*** 2.32****	5.1 4.2
4	2.1500 mg./cc. dextrose	Copper Reduction	2.15	0
5	2.1500 mg./cc. dextrose 0.5 M H_3PO_4	Copper Reduction	2.07*** 2.11****	-3.72 -1.86
6	2.1500 mg./cc. dextrose 2.15 mg./cc. sorbitol	Copper Reduction	2.09****	-2.79
	1.72 mg./cc. NaH_2PO_4 0.7 mg./cc. 85% H_3PO_4	Spectrophotometric	2.22	3.25

*Willstäter and Schudel Method.

**Kline and Acree Method.

***Neutralizing base added to Soxhlet Reagent.

****Neutralizing base added to sugar solution.

Table 17. Spectrophotometric Determination of Dextrose Using Dextrose-Carbazole Reaction*

Part I. Variation of Transmittance with Wavelength in the Range 350-700 mu.

A. Dextrose Concentration: 0.05 mg./cc.

L	T	A	L	T	A
350	7.0	1.155	465	84.8	0.071
360	35.0	0.456	470	85.0	0.071
370	65.0	0.187	475	85.0	0.071
380	74.5	0.128	480	84.8	0.071
390	77.5	0.111	485	84.0	0.076
395	78.8	0.104	500	80.2	0.096
400	79.8	0.098	520	72.1	0.142
405	80.0	0.097	525	70.2	0.154
410	80.5	0.094	530	69.2	0.160
415	80.8	0.093	535	69.0	0.161
420	81.2	0.090	540	69.3	0.160
425	81.5	0.089	545	70.8	0.150
430	82.8	0.082	550	72.9	0.138
435	82.8	0.082	560	79.0	0.103
440	83.2	0.080	580	88.7	0.053
445	83.8	0.077	600	92.5	0.034
450	84.0	0.076	620	94.5	0.025
455	84.5	0.073	650	95.5	0.021
460	84.8	0.071	700	96.5	0.016

B. Dextrose Concentration: 0.1 mg./cc.

350	5.8	1.237	530	50.5	0.297
380	66.0	0.181	535	50.0	0.301
400	75.0	0.126	540	50.5	0.297
420	76.5	0.117	545	53.0	0.276
440	77.0	0.114	550	56.3	0.249
460	77.5	0.111	555	61.0	0.215
480	76.8	0.115	560	66.5	0.178
500	68.2	0.167	580	83.0	0.081
510	61.5	0.211	600	91.0	0.041
520	55.0	0.260	650	95.5	0.020
525	52.5	0.280	700	97.0	0.013

Table 17. (Cont'd.) Spectrophotometric Determination of Dextrose Using Dextrose-Carbazole Reaction*

Part I. (Cont'd.)

C. Dextrose Concentration: 0.15 mg./cc.

L	T	A	L	T	A
350	4.0	1.398	480	68.2	0.166
390	62.5	0.204	500	58.5	0.233
400	67.0	0.174	520	44.0	0.356
405	68.5	0.164	525	41.0	0.387
410	69.0	0.161	530	39.2	0.407
430	69.0	0.161	535	38.5	0.414
435	69.0	0.161	540	39.0	0.410
440	69.0	0.161	545	41.5	0.382
445	69.0	0.161	550	44.8	0.348
450	69.5	0.158	570	67.0	0.174
455	69.5	0.158	590	81.5	0.089
460	69.5	0.158	610	87.8	0.056
465	69.5	0.158	650	91.5	0.039
470	69.5	0.158	700	92.8	0.032
475	69.2	0.160			

D. Dextrose Concentration: 0.2 mg./cc.

350	3.0	1.523	530	29.8	0.526
370	38.5	0.314	535	28.9	0.539
390	54.5	0.264	540	29.5	0.530
400	60.2	0.220	545	31.5	0.502
410	62.5	0.204	550	35.0	0.456
430	62.2	0.206	570	60.2	0.221
440	62.2	0.206	590	78.2	0.107
450	62.2	0.206	610	85.8	0.066
460	62.2	0.206	630	88.5	0.053
470	62.2	0.206	650	90.0	0.046
480	61.0	0.215	670	91.0	0.041
500	49.8	0.303	690	92.0	0.037
520	34.2	0.466	700	91.8	0.038

*L = Wavelength in mu.
T = Per cent transmittance.
A = Absorbance (optical density), i.e., $A = \log_{10}(100/T)$.

Table 17. (Cont'd.) Spectrophotometric Determination of Dextrose Using Dextrose-Carbazole Reaction

Part II. Transmittance as a Function of Concentration at 5.35 mu.

Concentration (mg./cc.)	T	Average T	A
0.05	68.0 67.8 69.3 69.2 70.0	68.9	0.162
0.1	50.5 50.5 51.5 51.0 49.2 50.5 52.3 48.5	50.5	0.297
0.15	39.0 39.0 38.8 38.0 39.2 39.2	38.9	0.411
0.175	34.2 34.0 33.8	34.0	0.469
0.2	30.0 29.2 31.5 30.5 29.2 31.0	30.2	0.521

Table 18. Summary of Exploratory Work on the Use of Chromatographic Adsorption Analysis for Sorbitol

Sample	Adsorbent	Developer	Sorbitol cm. from top	Zone length in cm.	Sorbitol Recovery (gms.)	(%)
0.2000 gms. Sorbitol Hydrate*	Attapulgus Clay** Dicalite	325 cc.*** of 85% isopropanol	-	-	0.1910	95.4
0.2000 gms. Sorbitol Hydrate	"	"	1.5	2.8	0.2000	100.0
0.2000 gms. Dextrose 0.1000 gms. Sorbitol Hydrate 0.120 gms. NaH_2PO_4 0.02 gms. NaOH	Florex XXX**** Celite 545	"	4.5	5.9	0.0985	98.5
1 cc. of Catholyte (at 8.25 hrs.) from Run No. 16	"	"	4.0	4.2	0.0380	-
1 cc. of Catholyte (at 8.25 hrs.) from Run No. 19	"	"	3.3 3.5	4.3 3.0	0.0267 0.0267	- -
1 cc. of Catholyte from Run No. 16	Attapulgus Clay-Dicalite	"	1.5	2.8	0.0380	-

*Sorbitol Hydrate is $C_6H_{14}O_6 \cdot \frac{1}{2} H_2O$, M. W. $\cong$ 191.

**The adsorbent consisted of 5 parts of minus 200 mesh attapulgus clay and 1 part dicalite filter aid. The adsorbent was prewashed and dried (isopropanol 85%).

***85% isopropanol by weight.

****The adsorbent consisted of 5 parts Florex XXX clay (90% passes through a 200 mesh screen) and 1 part celite 545. No pretreatment of the adsorbent was used.

Table 19. pH of NaH_2PO_4-NaOH Buffer Solutions*

Molarity of NaH_2PO_4	Normality of NaOH	pH
0.5	0.1	5.45
	0.2	5.90
	0.3	6.35
	0.4	6.80
	0.5	8.80
1.0	0.1	4.89
	0.3	5.60
	0.4	5.81
	0.5	6.08
	0.6	6.31
	0.7	6.58
	0.8	6.90
1.5	0.3	5.10
	0.4	5.30
	0.5	5.45
	0.7	5.80
	1.0	6.45
	1.1	6.58
	1.2	6.85
2.0	0.5	5.20
	0.6	5.35
	0.8	5.60
	1.0	5.90
	1.2	6.18
	1.4	6.49
	1.6	6.85
	1.4 (No Dextrose)	6.81

*All solutions contain 325 g./l. of dextrose.

Table 20. Cathode Potential* vs. Current Density

I. System: 325 g./l. Dextrose
120 g./l. NaH_2PO_4
30 g./l. NaOH

Temperature: 122°F.

Initial pH: 6.55

Current Density (amps./dm^2)	Cathode Potential* (volts)	Cell Volts
0	0.1958	1.40
0.283	1.428	3.01
0.417	1.491	3.20
0.610	1.627	3.50
0.800	1.675	3.78
1.000	1.702	3.95
1.333	1.722	4.12
1.666	1.741	4.31
2.000	1.764	4.50
2.417	1.790	4.80
3.000	1.853	4.99

II. System: 25 g./l. Dextrose
120 g./l. NaH_2PO_4
30 g./l. NaOH

Temperature: 122°F.

Initial pH: 6.85

0	0.0968	1.30
0.307	1.5600	3.18
0.377	1.5908	3.31
0.503	1.6250	3.49
0.653	1.631	3.68
0.767	1.646	3.80
0.833	1.650	3.85
1.000	1.661	3.95
1.333	1.685	4.10
1.667	1.711	4.29
2.133	1.718	4.49
2.533	1.762	4.78

Table 20. (Cont'd.) Cathode Potential* vs. Current Density

III. System: 325 g./l. Dextrose
120 g./l. NaH_2PO_4
0 g./l. NaOH

Temperature: 120°F.

Initial pH: 3.78

Current Density (amps./dm^2)	Cathode Potential* (volts)	Cell Volts
0	0.0555	1.30
0.050	1.2515	2.70
0.083	1.3048	2.80
0.122	1.3703	2.95
0.240	1.4295	3.11
0.327	1.4575	3.22
0.450	1.4902	3.43
0.560	1.5238	3.60
0.660	1.5447	3.72
0.742	1.5648	3.90
1.000	1.5967	4.10
1.333	1.6350	4.32
1.666	1.654	4.55
2.000	1.678	4.72
2.500	1.695	4.99
3.000	1.715	5.25

*Cathode Potential indicates the actual potentiometer reading of the cell consisting of the saturated calomel electrode and the cathode of the electrolytic cell.

Table 21. Change in pH of NaH_2PO_4 - NaOH Solutions* With the Addition of H_3PO_4

Molarity of NaH_2PO_4	Total Moles H_3PO_4 added/liter	pH
0.5	0	6.80
	0.046	6.50
	0.092	6.30
	0.138	6.09
	0.184	5.90
	0.230	5.71
	0.276	5.59
	0.368	5.20
1.0	0	6.90
	0.046	6.70
	0.092	6.35
	0.161	6.17
	0.299	5.85
	0.483	5.35
1.5	0	6.58
	0.046	6.45
	0.092	6.35
	0.184	6.15
	0.276	6.00
	0.368	5.85
	0.552	5.55
	0.644	5.40
	0.736	5.26
	0.828	5.10
2.0	0	6.85
	0.046	6.80
	0.138	6.65
	0.230	6.40
	0.322	6.25
	0.414	6.10
	0.506	6.00
	0.598	5.90
	0.690	5.75
	0.782	5.60
	0.874	5.50
	1.058	5.25

*All solutions contain 325 g./l. dextrose.

Table 22. Data for Run No. 7-Buffered Catholyte

Current Density.....1.05 amps./dm^2

Catholyte Composition.....325 g./l. dextrose, 1 M NaH_2PO_4, 0.25 NaOH

Anolyte Composition.....4 M H_3PO_4

Time (hrs.)	Concentration (g./l.)	Temperature (°F.)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)
0	325.0	116	5.40	0	-
0.5	308.5	116	5.20	5.2	96.9
1.0	299.0	116	5.22	7.5	69.3
2.0	291.0	116	5.25	9.2	42.6
3.0	280.0	116	5.25	12.4	38.3
4.0	276.0	116	5.30	13.3	30.7
6.0	262.5	116	5.38	17.2	26.6
8.0	254.0	116	5.58	18.8	21.7
10.0	244.0	120	5.65	21.8	20.2

Table 23. Data for Run No. 8-Buffered Catholyte

Current Density.....1.02 amps./dm^2

Catholyte Composition.....319 g./l. dextrose, 1 M NaH_2PO_4, 0.25 M NaOH

Anolyte Composition.....4 M H_3PO_4

Time (hrs.)	Concentration (g./l.)	Temperature (°F.)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)
0	319.0	116	5.52	0	-
0.5	302.0	118	5.40	5.1	95.2
1.0	296.5	118	5.32	6.7	62.0
2.0	288.0	121	5.42	9.3	43.2
3.0	280.5	121	5.45	11.8	36.6
4.0	276.0	122	5.50	13.0	30.2
6.0	266.5	121	5.60	15.3	23.7
8.0	256.5	121	5.70	18.1	21.0
10.0	245.0	121	5.80	21.4	19.9

Table 24. Data for Run No. 9-Buffered Catholyte

Current Density.....0.81 amps./dm^2

Catholyte Composition.....323 g./l. dextrose, 1 M NaH_2PO_4, 0.25 M NaOH

Anolyte Composition.....4 M H_3PO_4

Time (hrs.)	Concentration (g./l.)	Temperature (°F.)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)
0	323.0	111	5.48	0	-
0.5	310.5	111	5.20	4.0	95.0
1.0	300.5	112	5.15	7.4	87.5
2.0	292.0	112	5.20	10.5	62.0
3.0	289.0	112	5.20	11.5	45.0
4.5	278.0	112	5.20	14.3	37.4
6.0	268.5	112	5.10	17.5	34.4
8.0	258.0	112	5.25	20.4	30.1

Table 25. Data for Run No. 10-Buffered Catholyte

Current Density.....0.81 amps./dm^2

Catholyte Composition.....323 g./l. dextrose, 1 M NaH_2PO_4, 0.25 M NaOH

Anolyte Composition.....4 M H_3PO_4

Time (hrs.)	Concentration (g./l.)	Temperature (°F.)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)
0	323.0	115	5.48	0	-
0.5	299.5	113	4.85	6.82	-
1.0	290.0	114	4.85	9.50	-
2.0	286.0	114	4.85	10.65	63.5
3.0	283.5	114	4.85	12.00	47.8
4.5	280.5	116	4.85	12.45	33.0
6.0	272.0	116	4.90	14.95	29.7
8.0	265.0	112	4.90	17.22	25.7

Table 26. Data for Run No. 11-Buffered Catholyte

Current Density.....0.83 amps./$dm.^2$

Catholyte Composition.....297 g./l. dextrose, 2 M NaH_2PO_4, 0.75 M NaOH

Anolyte Composition.....4 M H_3PO_4

Time (hrs.)	Concentration (g./l.)	Temperature ($^{o}F.$)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)
0	297.0	118	5.70	-	-
0.5	268.0	116	5.30	10.6	-
1.0	259.0	115	5.30	14.4	-
2.0	254.5	114	5.32	16.2	86.4
3.0	250.0	112	5.35	17.6	62.7
4.5	245.0	112	5.48	19.5	46.5
6.0	238.5	112	5.50	21.4	38.2
8.0	231.0	112	5.62	23.8	31.7

Table 27. Data for Run No. 12-Buffered Catholyte

Current Density.....0.81 amps./dm^2

Catholyte Composition.....323 g./l. dextrose, 1.3 M NaH_2PO_4, 0.75 M NaOH

Anolyte Composition.....4 M H_3PO_4

Time (hrs.)	Concentration (g./l.)	Temperature (°F.)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)
0	323.0	121	6.20	-	-
0.5	302.0	121	5.95	6.7	-
1.0	299.0	118	5.90	7.8	92.0
2.0	290.0	117	5.90	10.4	62.0
3.0	282.0	117	5.90	12.2	48.4
4.5	273.0	117	5.95	15.2	40.2
6.0	262.0	117	6.02	18.6	36.9
8.0	250.0	117	6.08	22.3	33.2

Table 28. Data for Run No. 15-Buffered Catholyte

Current Density.....0.80 amps/dm^2

Catholyte Composition.....305 g./l. Dextrose,
1 M NaH_2PO_4, 0.875 M NaOH

Anolyte Composition.....4 M H_3PO_4

Time (hrs.)	Current Density (amps./dm^2)	Concentration (g./l.)	Temperature (°F.)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)
0	2.67	305.0	121	7.08	-	-
0.25	0.80	289.5	121	6.80	6.9	93.4
1.75	0.80	268.0	121	6.25	11.7	56.6
3.25	0.80	254.0	120	6.12	16.0	47.4
5.25	0.80	237.0	120	6.20	21.5	41.9
6.75	0.80	225.0	120	6.30	25.5	39.4
8.25	0.80	210.5	121	6.20	29.9	38.4

Table 29. Data for Run No. 16-Buffered Catholyte

Current Density.....0.65 amps./dm^2

Catholyte Composition.....277 g./l. Dextrose,
1 M NaH_2PO_4, 0.875 M NaOH

Anolyte Composition.....4 M H_3PO_4

Time (hrs.)	Current Density (amps./dm^2)	Concentration (g./l.)	Temperature (°F.)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)
0	2.50	277.0	126	7.07	-	-
0.25	0.65	253.0	123	6.30	7.7	66.5
1.75	0.65	235.0	119	6.60	16.0	68.0
3.25	0.65	219.0	118	6.70	22.1	62.7
5.25	0.65	201.0	118	6.68	28.4	55.5
6.75	0.65	183.5	118	6.80	34.5	55.0
8.25	0.65	167.0	118	6.80	40.3	54.0

Table 30. Data for Run No. 18-Buffered Catholyte

Current Density.....0.65 amps./dm^2

Catholyte Composition.....318 g./l. Dextrose, 1 M NaH_2PO_4, 0.875 M NaOH

Anolyte Composition.....4 M H_3PO_4

Time (hrs.)	Current Density (amps./dm^2)	Concentration (g./l.)	Temperature ($^oF.$)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)
0	2.50	318.0	118	7.02	-	-
0.33	0.65	300.0	120	6.38	6.9	-
1.83	0.65	281.0	120	6.40	12.0	82.8
3.33	0.65	265.0	118	6.38	16.6	67.0
5.33	0.65	249.0	119	6.55	21.8	56.5
8.33	0.65	220.0	118	6.63	30.4	51.5
11.33	0.65	193.5	120	6.72	39.2	49.0

Table 31. Data for Run No. 19-Buffered Catholyte

Current Density.....0.65 amps./dm^2

Catholyte Composition.....326 g./l. Dextrose, 1 M NaH_2PO_4, 0.875 M NaOH

Anolyte Composition.....4 M H_3PO_4

Time (hrs.)	Current Density ($amps./dm^2$)	Concentration (g./l.)	Temperature (°F.)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)
0	2.50	326.0	121	7.00	-	-
0.25	0.65	299.0	123	6.40	10.3	-
1.75	0.65	279.0	121	6.30	16.5	-
3.25	0.65	263.0	120	6.20	21.0	79.0
5.00	0.65	250.0	119	6.28	24.9	65.0
6.75	0.65	237.0	119	6.30	28.2	56.4
8.25	0.65	226.0	120	6.40	31.4	52.4

Table 32. Data for Run No. 22-Buffered Catholyte

Current Density.....0.65 amps./dm^2

Catholyte Composition.....326 g./l. Dextrose, 1 M NaH_2PO_4, 0.75 M NaOH

Anolyte Composition.....4 M H_3PO_4

Time (hrs.)	Current Density (amps./dm^2)	Cathode Potential* (volts)	Concentration (g./l.)	Temperature (°F.)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)
0	2.50	1.757	326.0	120	6.55	0	-
0.08	0.65	1.635	311.0	120	5.95	4.5	-
1.08	0.65	1.602	294.0	120	5.85	9.5	-
2.08	0.65	1.605	281.0	119	6.03	13.1	83.0
3.50	0.65	1.607	264.5	119	5.95	18.0	71.0
5.00	0.65	1.612	256.0	118	6.02	20.6	58.2
6.00	0.65	1.615	244.5	118	6.00	24.2	57.4
8.08	0.65	1.625	228.0	118	5.92	29.6	52.7

*Cathode Potential indicates the actual potentiometer reading of the cell consisting of the saturated calomel electrode and the cathode of the electrolytic cell.

Table 33. Data for Run No. 23-Buffered Catholyte

Current Density.....0.65 amps./dm^2

Catholyte Composition.....325 g./l. dextrose, 1 M NaH_2PO_4, 0.75 M NaOH

Anolyte Composition.....4 M H_3PO_4

Time (hrs.)	Current Density (amps./dm^2)	Cathode Potential* (volts)	Concentration (g./l.)	Temperature (°F.)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)
0	0.65	1.632	325.0	120	6.55	-	-
1.0	0.65	1.657	301.0	119	6.18	6.6	97.8
2.5	0.65	1.698	286.0	118	6.28	11.4	67.6
4.0	0.65	1.725	267.5	118	6.35	17.6	65.2
6.0	0.65	1.730	242.0	118	6.55	25.6	63.5
8.0	0.65	1.622	209.0	118	6.75	35.9	66.7

*See definition in Table 32.

Table 34. Data for Run No. 24-Buffered Catholyte

Current Density.....0.65 amps./dm^2

Catholyte Composition.....330 g./l. Dextrose,
1 M NaH_2PO_4, 0.75 M NaOH

Anolyte Composition.....4 M H_3PO_4

Time (hrs.)	Current Density (amps./dm^2)	Cathode Potential* (volts)	Concentration (g./l.)	Temperature (°F.)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)
0	2.50	1.808	331.0	123	6.55	-	-
0.42	0.65	1.616	297.0	130	6.18	9.1	85.6
1.00	0.65	1.643	284.0	124	6.19	12.7	87.8
2.00	0.65	1.658	271.5	120	6.22	17.1	81.1
3.50	0.65	1.690	254.0	120	6.13	22.5	72.8
5.00	0.65	1.713	237.0	119	6.50	27.8	68.0
7.00	0.65	1.735	210.0	119	6.62	36.2	67.1
8.42	0.65	1.735	190.5	119	6.68	42.0	66.6

*See definition in Table 32.

Table 35. Data for Run No. 25-Buffered Catholyte

Current Density.....0.65 amps./dm^2

Catholyte Composition.....326 g./l. Dextrose, 1 M NaH_2PO_4, 0.75 M NaOH

Anolyte Composition.....4 M H_3PO_4

Time (hrs.)	Current Density (amps./dm^2)	Cathode Potential* (volts)	Concentration (g./l.)	Temperature (°F.)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)
0	0.65	1.654	326	118	6.55	-	-
1.0	0.65	1.644	301	118	5.68	7.0	-
2.0	0.65	1.650	291	118	6.13	9.7	72.4
3.5	0.65	1.666	276	118	6.13	14.6	62.4
5.0	0.65	1.695	266	118	6.17	17.4	52.0
6.5	0.65	1.699	250	118	6.23	22.7	52.0
8.0	0.65	1.725	233	118	6.51	28.4	52.9

*See definition in Table 32.

Table 36. Data for Run No. 26-Buffered Catholyte

Current Density.....0.65 amps./dm^2

Catholyte Composition.....327 g./l. Dextrose, 1 M NaH_2PO_4, 0.125 M NaOH

Anolyte Composition.....4 M H_3PO_4

Time (hrs.)	Current Density (amps./dm^2)	Cathode Potential* (volts)	Concentration (g./l.)	Temperature (°F.)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)
0	2.50	1.669	327.0	118	4.95	-	-
0.42	0.65	1.500	307.5	126	4.95	4.4	40.8
1.00	0.65	1.512	293.0	121	4.75	8.6	59.0
2.00	0.65	1.507	287.0	119	4.55	9.2	41.2
4.00	0.65	1.514	279.0	117	4.90	12.6	36.3
6.00	0.65	1.535	269.0	117	4.89	15.8	33.0
8.42	0.65	1.558	254.5	117	5.11	20.5	31.9

*See definition in Table 32.

Table 37. Data for Run No. 27-Buffered Catholyte

Current Density.....0.65 amps./dm^2

Catholyte Composition.....325 g./l. Dextrose,
1 M NaH_2PO_4, 0.125 M NaOH

Anolyte Composition.....4 M H_3PO_4

Time (hrs.)	Current Density (amps./dm^2)	Cathode Potential* (volts)	Concentration (g./l.)	Temperature (°F.)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)
0	0.65	1.470	325.0	120	4.95	-	-
1	0.65	1.471	306.0	120	4.90	4.8	72.0
2	0.65	1.485	297.0	118	4.89	8.3	61.0
4	0.65	1.514	287.0	117	4.92	11.2	41.6
6	0.65	1.472	282.0	118	5.19	13.5	33.3
8	0.65	1.489	272.0	117	5.15	16.5	31.1

*See definition in Table 32.

Table 38. Data for Run No. 28-Buffered Catholyte

Current Density.....1.00 amps./dm^2

Catholyte Composition.....329 g./l. Dextrose, 1 M NaH_2PO_4, 0.5 M NaOH

Anolyte Composition.....4 M H_3PO_4

Time (hrs.)	Current Density (amps./dm^2)	Cathode Potential* (volts)	Concentration (g./l.)	Temperature (°F.)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)
0	2.50	1.709	329.0	122	5.94	-	-
0.42	1.00	1.620	303.0	130	5.75	5.1	47.5
1.00	1.00	1.620	294.0	125	5.70	7.6	45.5
2.00	1.00	1.610	282.0	122	5.79	10.4	38.5
3.50	1.00	1.629	263.0	121	5.89	16.4	38.6
5.00	1.00	1.642	251.0	121	5.75	19.8	34.3
6.50	1.00	1.662	236.5	121	5.95	34.3	33.2
8.42	1.00	1.680	215.0	122	6.05	30.7	33.1

*See definition in Table 32.

Table 39. Data for Run No. 29-Buffered Catholyte

Current Density.....0.45 amps./dm^2

Catholyte Composition.....326 g./l. Dextrose, 1 M NaH_2PO_4, 0.75 M NaOH

Anolyte Composition.....4 M H_3PO_4

Time (hrs.)	Current Density (amps./dm^2)	Cathode Potential* (volts)	Concentration (g./l.)	Temperature (°F.)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)
0	2.50	1.718	326.0	123	6.60	-	-
0.42	0.45	1.426	298.0	130	6.45	8.0	74.3
1.00	0.45	1.444	291.0	122	6.25	10.2	75.8
2.00	0.45	1.459	284.0	118	6.22	12.6	69.6
3.50	0.45	1.464	273.5	118	6.26	16.1	64.0
5.00	0.45	1.472	264.0	117	6.28	18.7	58.3
6.50	0.45	1.477	256.5	116	6.22	21.2	54.5
8.42	0.45	1.480	246.5	114	6.32	24.0	50.0

*See definition in Table 32.

Table 40. Data for Run No. 30-Buffered Catholyte

Current Density.....1.25 amps./dm^2

Catholyte Composition.....329 g./l. Dextrose, 1 M NaH_2PO_4, 0.5 M NaOH

Anolyte Composition.....4 M H_3PO_4

Time (hrs.)	Current Density (amps./dm^2)	Cathode Potential* (volts)	Concentration (g./l.)	Temperature (°F.)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)
0	2.50	1.675	329.0	119	6.03	-	-
0.42	1.25	1.543	307.0	126	5.81	5.9	55.3
1.00	1.25	1.554	296.5	122	5.80	9.4	52.0
2.00	1.25	1.586	282.5	122	6.02	13.8	44.8
3.50	1.25	1.620	268.0	122	6.19	18.0	36.0
5.00	1.25	1.648	253.0	122	6.25	22.4	32.5
6.50	1.25	1.721	232.5	122	6.55	28.6	32.5
8.42	1.25	1.746	197.5	124	6.89	39.4	35.0

*See definition in Table 32.

Table 41. Data for Run No. 31
Electroendosmosis of 4 M H_3PO_4 Anolyte
Temperature of Anolyte-120°F.

Time (hrs.)	Current Density (amps./dm^2)	Bulk Catholyte pH	Cathode Potential* (volts)
0	0	7.03	0.281
0	2.5	7.03	-
0.083	2.5	-	1.854
0.200	2.5	-	1.824
0.291	2.5	-	1.804
0.392	2.5	-	1.794
0.417	2.5	6.85	1.449
0.634	0.65	-	1.551
0.750	0.65	6.87	1.550
0.933	0.65	-	1.547
1.000	0.65	6.93	-
1.167	0.65	-	1.556
1.333	0.65	7.00	1.562
1.417	2.50	-	-
1.450	2.50	-	1.846
1.500	2.50	7.06	-
1.583	2.50	7.15	1.794
1.733	2.50	-	1.643
1.750	2.50	7.37	-
1.800	2.50	-	1.674
1.833	0.65	7.95	-
1.900	0.65	-	1.459
1.968	0.65	-	1.491
2.000	0.65	7.75	-
2.133	0.65	-	1.497
2.166	0.65	7.68	-
2.300	0.65	-	1.488
2.400	0.65	-	1.487
2.417	0.65	7.32	-
2.666	0.65	7.06	-
2.717	0.65	-	1.478
2.833	0.65	-	1.495
3.083	0.65	6.71	-
3.117	0.65	-	1.488
3.367	0.65	6.50	-
3.417	0.65	-	1.473
3.583	0.65	6.50	-

*See definition in Table 32.

Table 42. Data for Run No. 32
Electroendosmosis of 2 M H_3PO_4 Anolyte
Temperature of Anolyte-120°F.

Time (hrs.)	Current Density (amps./dm^2)	Bulk Catholyte pH	Cathode Potential* (volts)
0	0	7.03	0.246
0	2.50	7.03	-
0.058	2.50	-	1.850
0.142	2.50	-	1.824
0.167	2.50	6.75	-
0.200	2.50	-	1.827
0.250	2.50	-	1.816
0.325	2.50	-	1.805
0.333	2.50	6.70	-
0.384	2.50	-	1.800
0.417	0.65	-	-
0.459	0.65	-	1.456
0.500	0.65	6.85	-
0.534	0.65	-	1.495
0.616	0.65	-	1.558
0.710	0.65	-	1.555
0.750	0.65	6.89	-
0.826	0.65	-	1.554
0.950	0.65	-	1.554
1.000	0.65	6.88	-
1.142	0.65	-	1.554
1.242	0.65	-	1.562
1.250	0.65	6.90	-
1.434	0.65	-	1.566
1.500	0.65	6.93	-
1.625	0.65	-	1.583
1.725	0.65	-	1.582
1.750	0.65	7.02	-
1.885	0.65	-	1.595
1.918	2.50	-	-
1.960	2.50	-	1.843
2.000	2.50	7.11	-
2.082	2.50	-	1.695
2.234	2.50	-	1.677
2.250	2.50	8.10	-
2.367	2.50	-	1.738
2.417	0.65	9.52	-
2.458	0.65	-	1.469
2.559	0.65	-	1.507
2.700	0.65	-	1.485
2.750	0.65	9.20	-
2.875	0.65	-	1.487
3.000	0.65	8.99	-

Table 42. (Cont'd.) Data for Run No. 32

Electrendosmosis of 2 M H_3PO_4 Anolyte

Time (hrs.)	Current Density (amps./dm^2)	Bulk Catholyte pH	Cathode Potential* (volts)
3.050	0.65	-	1.487
3.242	0.65	-	1.487
3.250	0.65	8.23	-
3.392	0.65	-	1.507
3.500	0.65	7.91	-
3.516	0.65	-	1.505
3.742	0.65	-	1.505
3.750	0.65	7.45	-
3.918	0.65	-	1.513
4.000	0.65	7.61	-
4.083	0.65	-	1.513
4.250	0.65	7.53	-
4.333	0.65	7.52	-
4.350	0.65	-	1.530
4.500	0.65	7.52	-

*See definition in Table 32.

Table 43. Data for Run No. 33-Buffered Catholyte

Current Density.....0.65 amps./dm^2

Catholyte Composition.....327 g./l. Dextrose, 1 M NaH_2PO_4, 0.75 M NaOH

Anolyte Composition.....4 M H_3PO_4

Time (hrs.)	Current Density (amps./dm^2)	Cathode Potential* (volts)	Concentration (g./l.)	Temperature (°F.)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)	Moles H_3PO_4 added
0	2.42	1.748	327	121	6.63	-	-	-
0.42	0.65	1.518	-	130	6.43	-	-	-
3.00	0.65	1.552	267	119	6.50	18.9	67.3	-
6.16	0.65	1.587	-	119	6.70	-	-	0.0074
7.00	0.65	1.591	229	120	6.50	30.2	55.1	-
7.16	0.65	1.591	-	120	6.50	-	-	0.0041
8.16	0.65	1.591	-	120	6.52	-	-	0.0041
9.30	0.65	1.607	-	120	6.68	-	-	0.0082
10.25	0.65	1.606	-	120	6.61	-	-	0.0070
11.00	0.65	1.604	192	120	6.40	40.9	50.3	-
12.08	0.65	1.623	-	120	6.68	-	-	0.0082
13.00	0.65	1.613	-	120	6.55	-	-	0.0041
14.00	0.65	1.622	-	120	6.52	-	-	0.0041
15.00	0.65	1.622	159	120	6.40	50.6	46.8	-
17.00	0.65	1.638	-	120	6.59	-	-	0.0041
20.00	0.65	1.651	131	120	6.50	59.4	42.2	-
21.00	0.65	1.653	-	120	6.65	-	-	0.0041
24.00	0.65	1.655	107	120	6.45	66.5	39.6	-

*See definition in Table 32.

Table 44. Data for Run No. 34-Unbuffered Acid Catholyte

Current Density.....1.00 amps./dm^2

Catholyte Composition.....325 g./l. Dextrose, 75 g./l. Na_2SO_4, 0.5 g./l. H_2SO_4

Anolyte Composition.....300 g./l. H_2SO_4

Time (hrs.)	Cathode Potential* (volts)	Concentration (g./l.)	Temperature (°F.)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)	Equiv. H_2SO_4 added
0	1.815	325.0	71	2.32	-	-	-
1.00	1.812	-	70	10.00	-	-	0.004
1.25	-	-	69	9.95	-	-	0.008
1.50	-	-	69	9.50	-	-	0.008
2.00	1.808	274.0	68	5.70	12.7	61.2	0.034
3.00	1.812	-	68	1.70	-	-	-
4.00	1.819	246.0	68	1.99	21.7	52.5	-
6.00	1.816	230.0	69	2.05	27.2	43.9	-
8.00	1.824	212.5	69	1.98	33.4	40.4	-

*See definition in Table 32.

Table 45. Data for Run No. 35-Alkaline Catholyte

Current Density.....1.00 amps./dm^2

Catholyte Composition.....324 g./l. Dextrose,
75 g./l. Na_2SO_4

Anolyte Composition.....300 g./l. H_2SO_4

Time (hrs.)	Cathode Potential* (volts)	Concentration (g./l.)	Temperature (°F.)	Catholyte pH	Reduction (%)	Apparent Current Efficiency (%)
0	1.760	324.0	68	6.01	-	-
2.00	1.814	277.0	68	9.90	14.0	67.5
4.00	1.812	251.0	68	10.18	22.9	55.1
6.00	1.812	216.0	68	10.30	33.5	54.1
8.00	1.813	183.5	68	10.10	43.8	50.4

*See definition in Table 32.

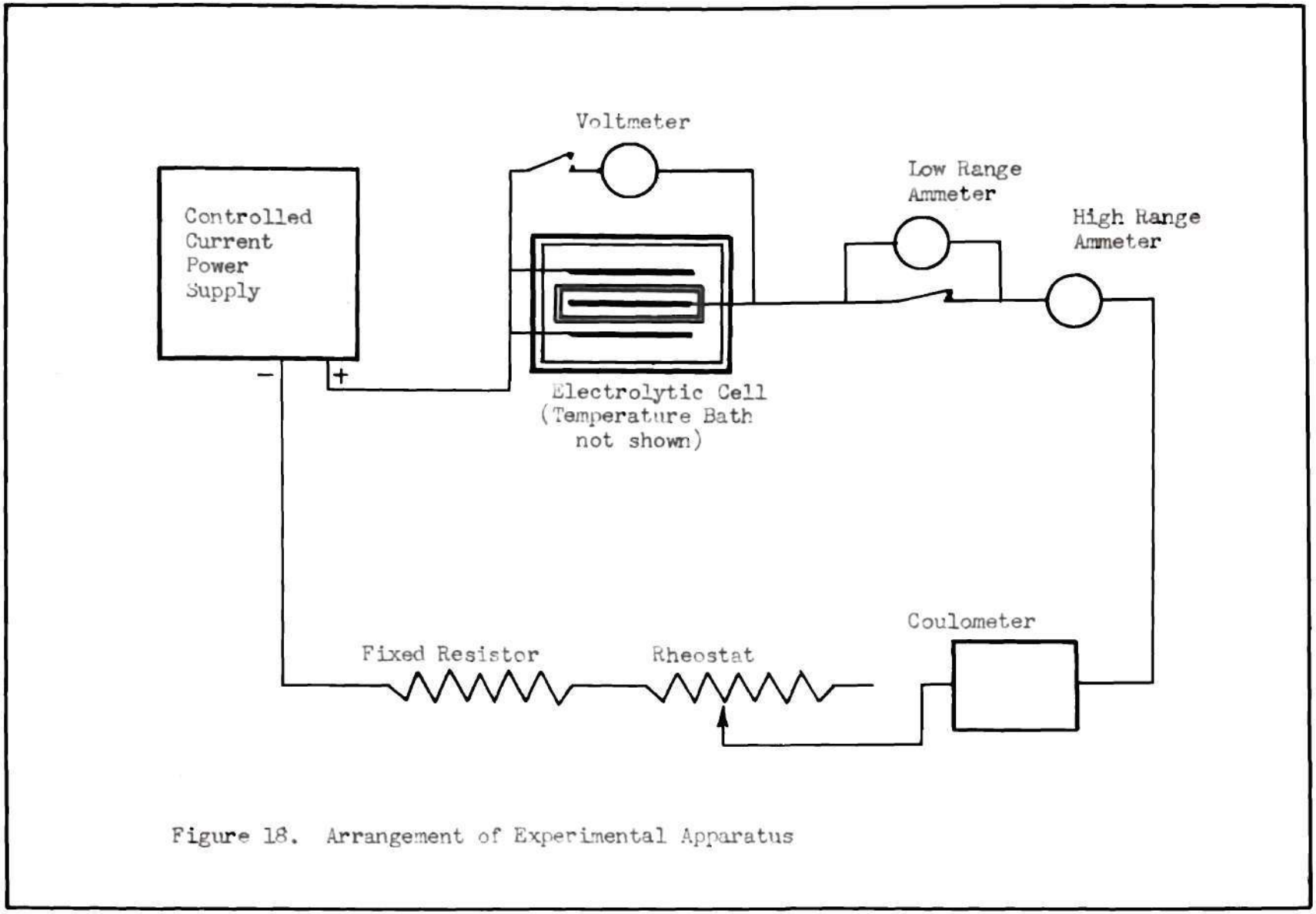
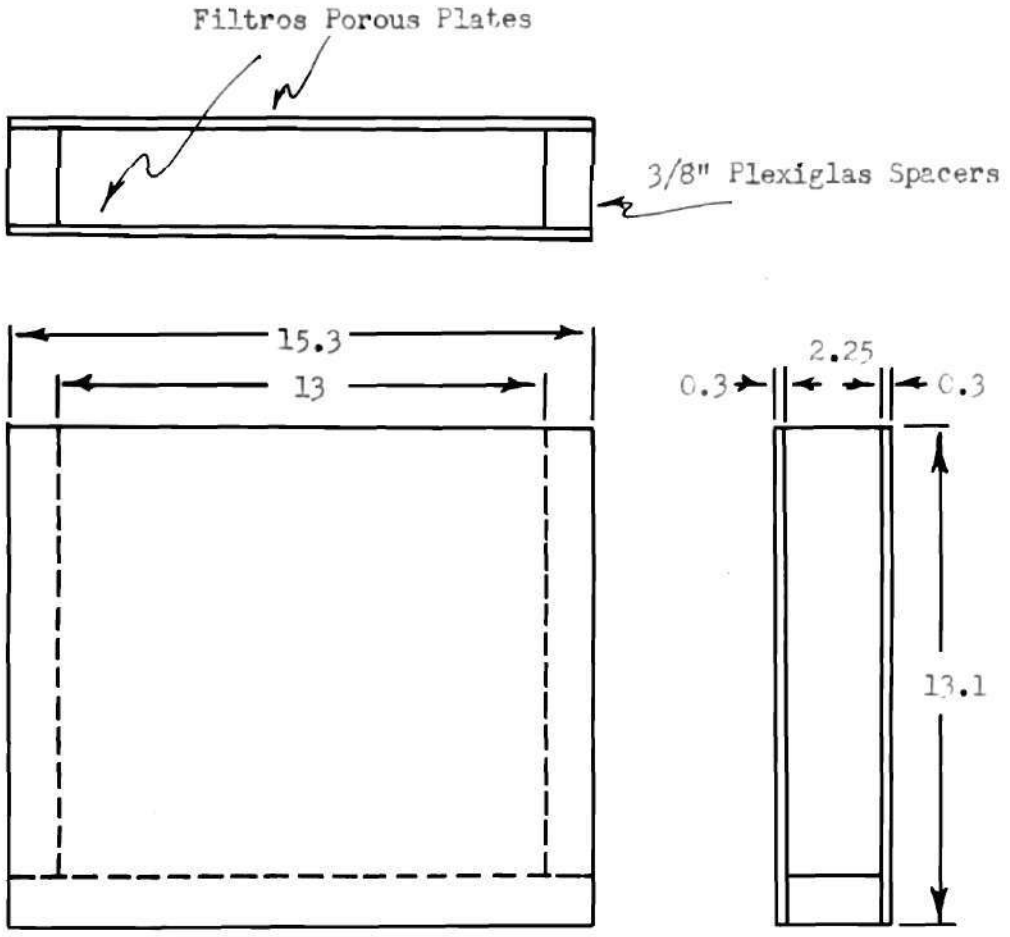
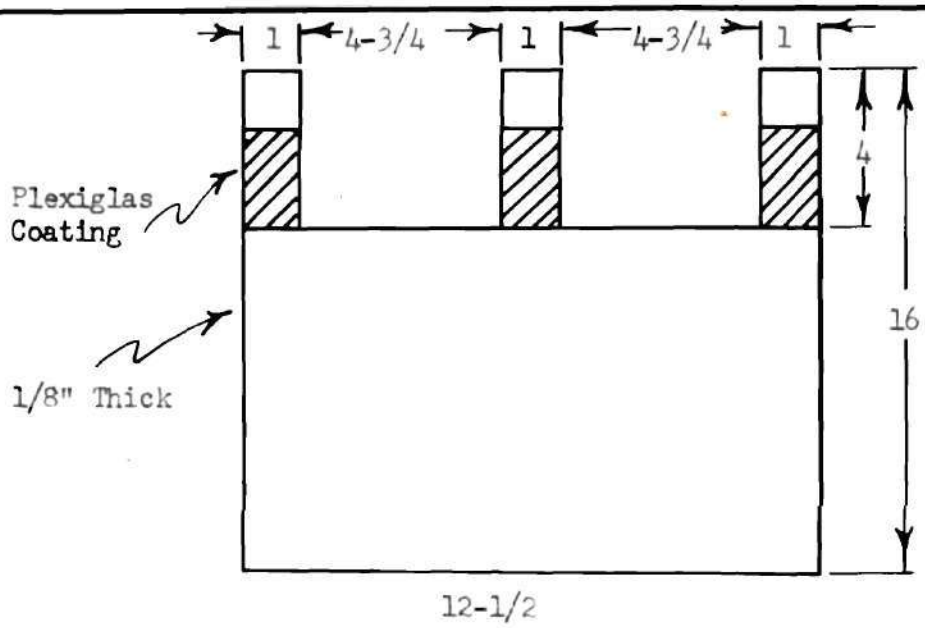


Figure 18. Arrangement of Experimental Apparatus



All dimensions are expressed in cm.

Figure 19. Construction of Electrolytic Diaphragm



All dimensions are expressed in cm.

Figure 20. Electrode Specifications

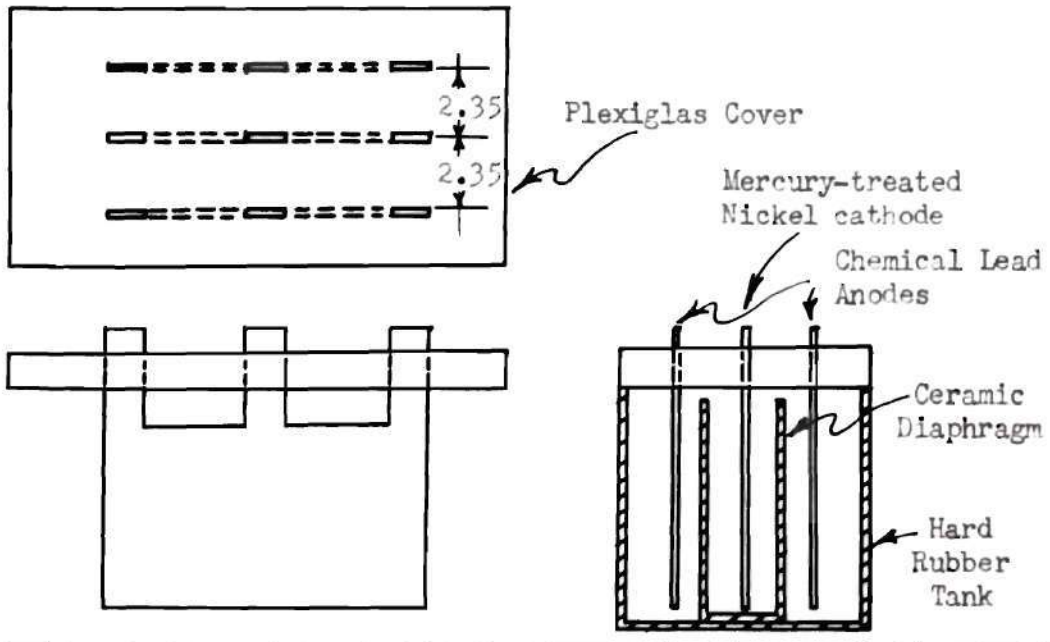


Figure 21. Arrangement of Electrodes in the Cell

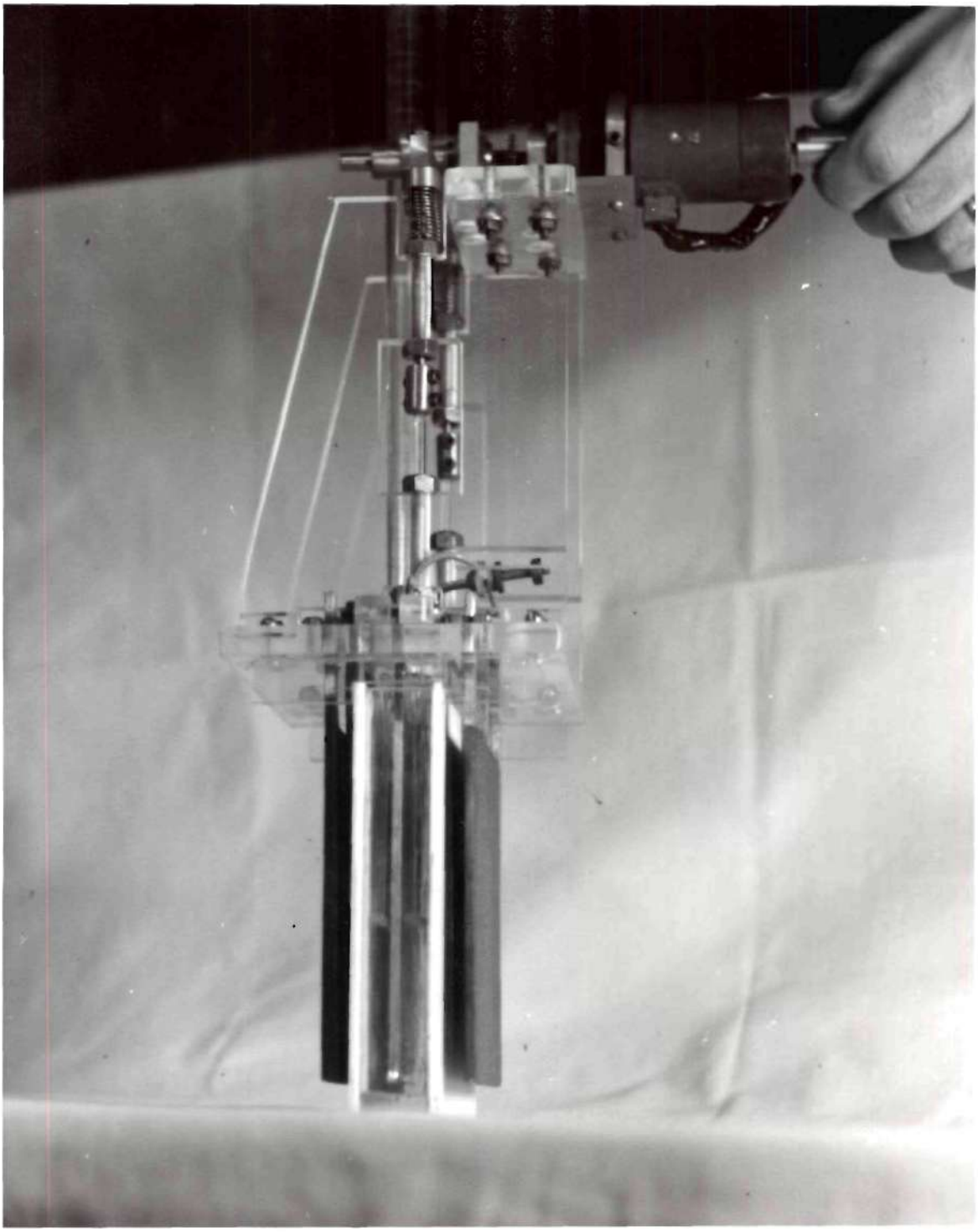


Figure 22. Assembled Cell, Anolyte Container Removed

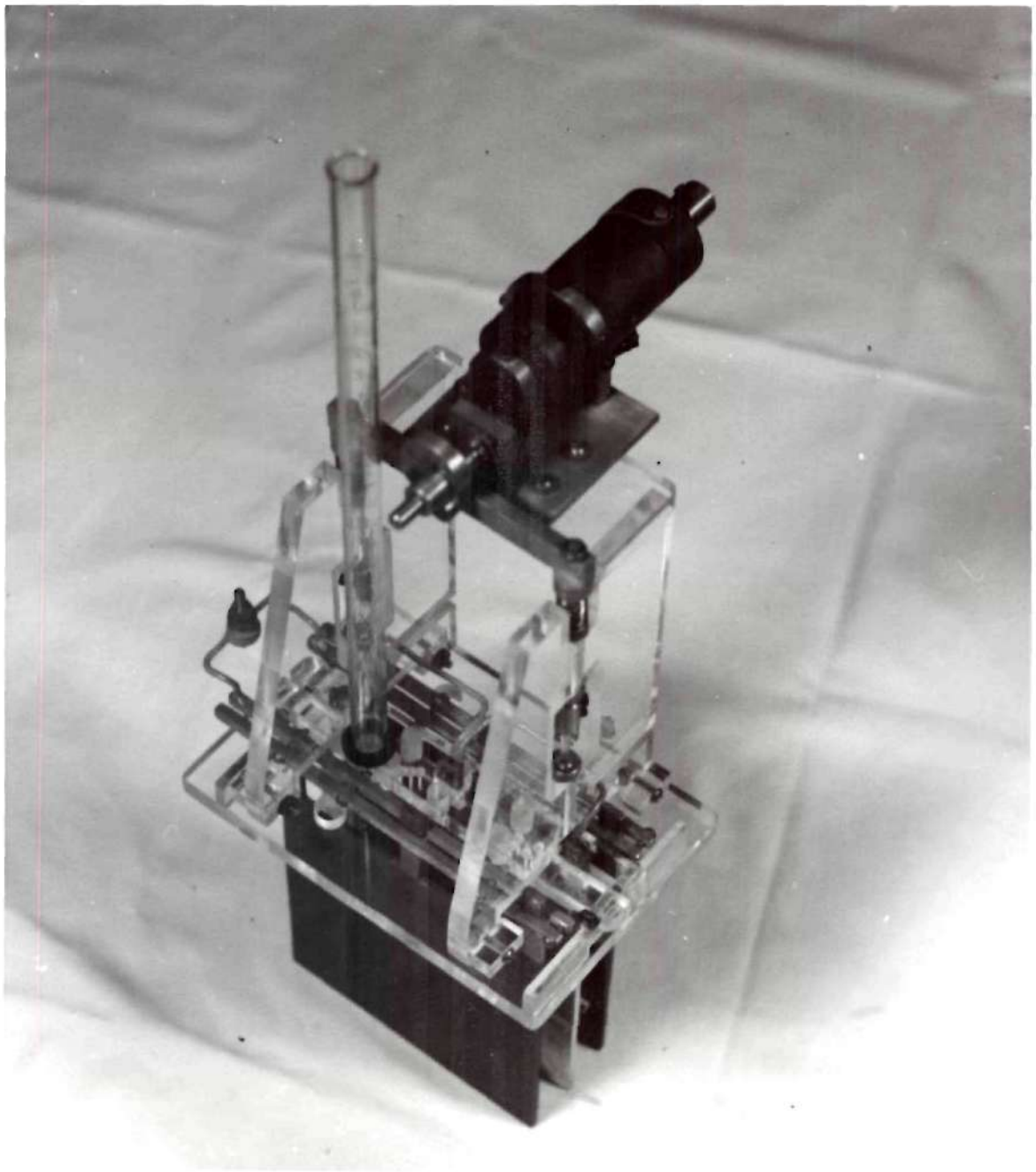


Figure 23. Agitating Mechanism

Figure 24. Assembled Cell

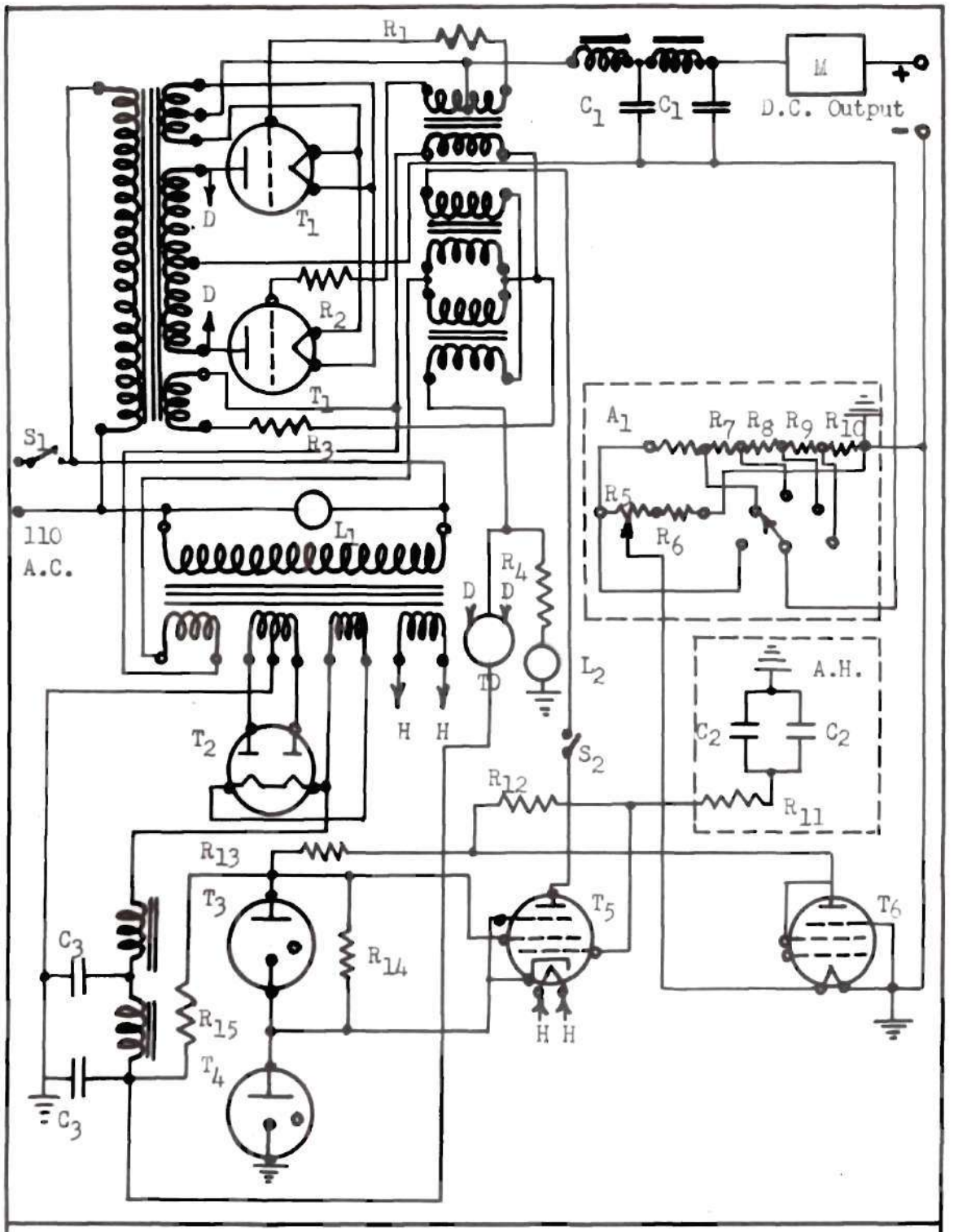


Figure 25. Controlled Current Power Supply

List of Parts for Controlled Current
Power Supply Shown in Figure 25.

R_1, R_2.....5,100 ohms
R_3.....24,500 ohms
R_4.....400,000 ohms
R_5.....25 ohms
R_6.....5 ohms
R_7.....0.5 ohms
R_8, R_9, R_{10}.....0.2 ohms
R_{11}.....65,000 ohms
R_{12}.....100,000 ohms
R_{13}.....10 megohms
R_{14}.....65,000 ohms
R_{15}.....8,000 ohms

C_1.....3,000 mfd, 50 volts
C_2, C_3.....4 mfd, 600 volts

T_1.....C6J thyratron
T_2.....5Y3
T_3, T_4.....VR-105
T_5.....6SH7
T_6.....1A5-GT

L_1.....main power indicator lamp
L_2.....regulating circuit lamp

T.D.....time delay relay

S_1.....main power switch
S_2.....regulating circuit switch

A_1.....Ayrton shunt
A.H.....anti-hunt" circuit

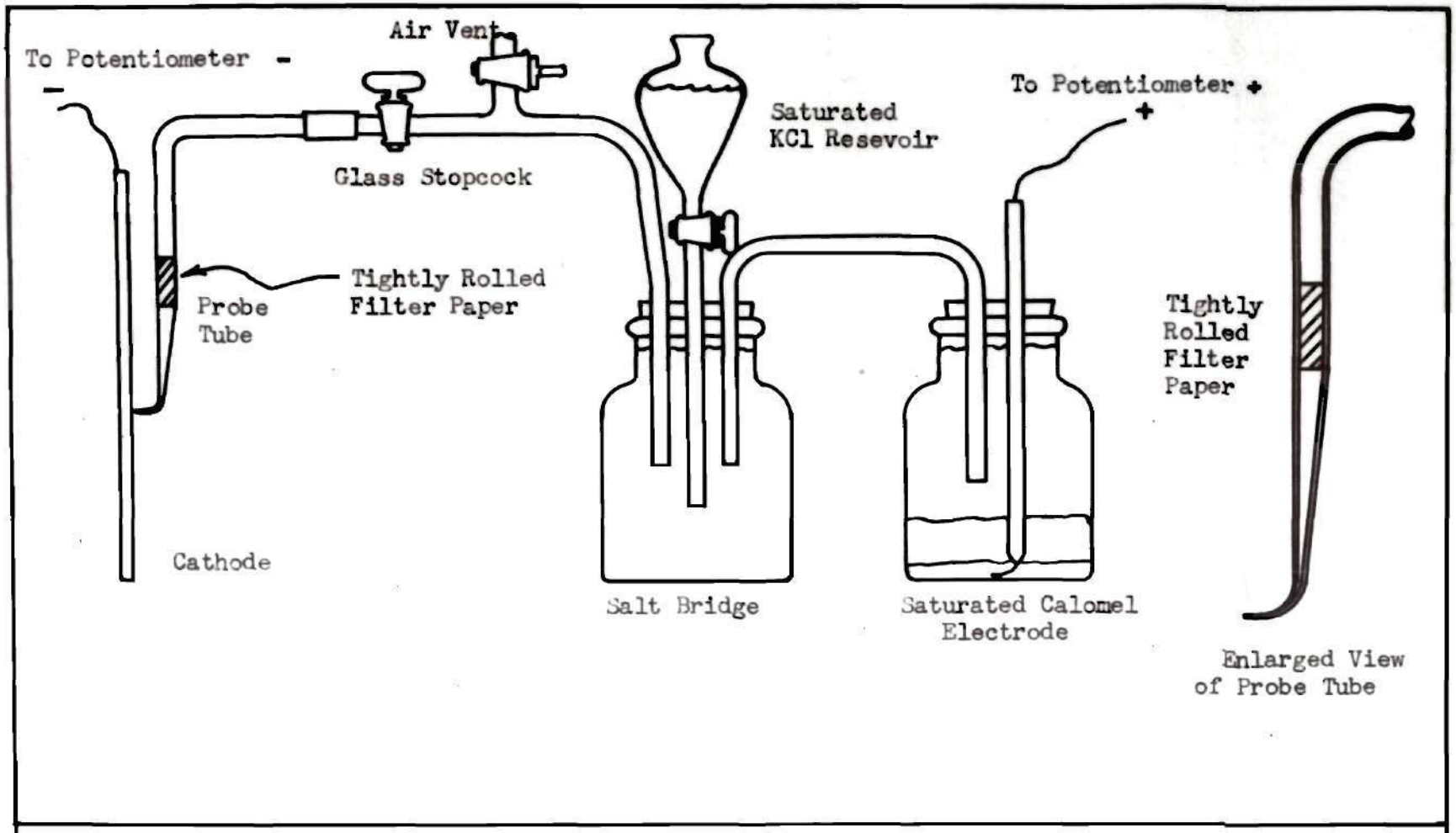


Figure 26. Arrangement for Measurement of Cathode Potential

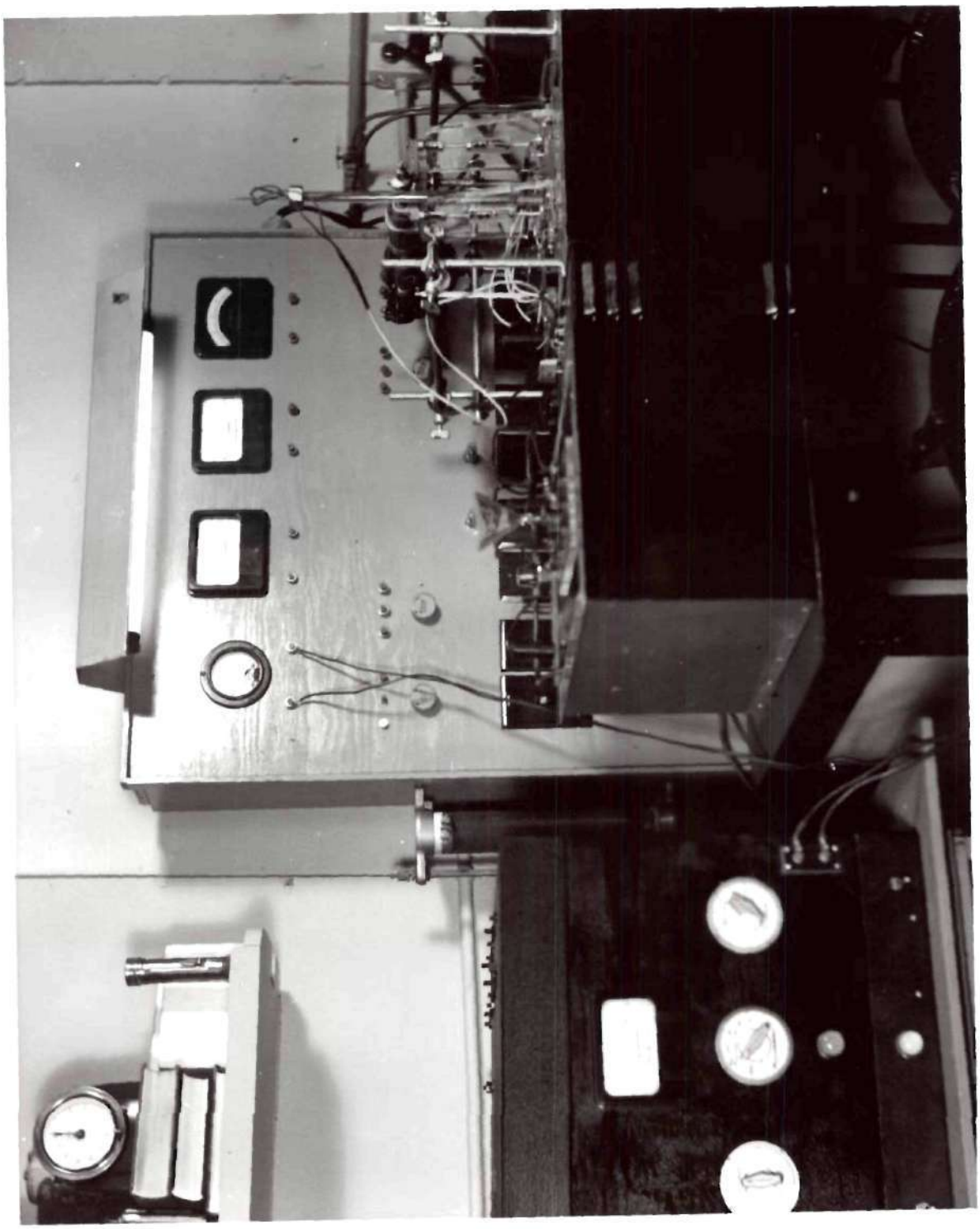


Figure 27. General View of Apparatus

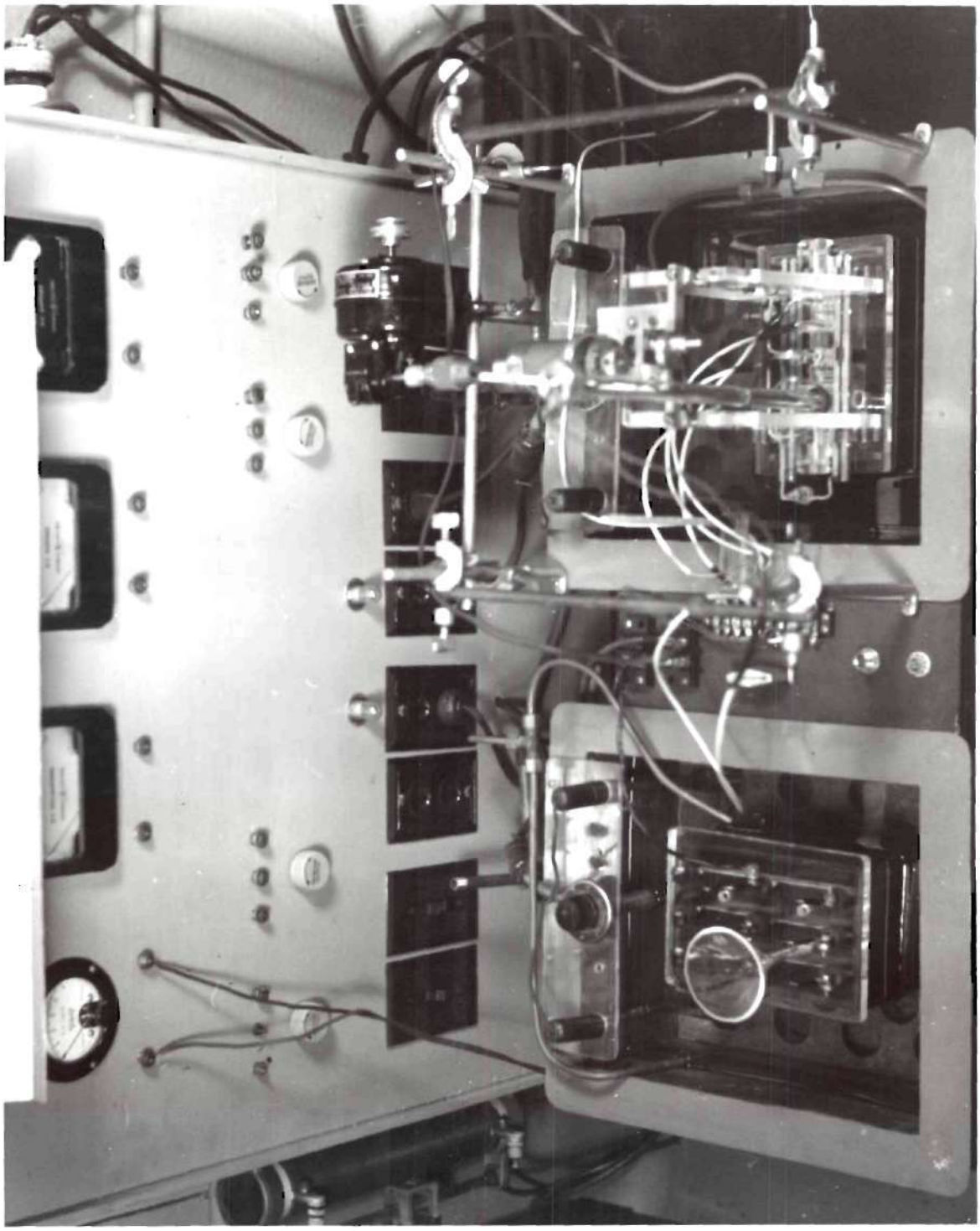


Figure 28. Enlarged View of Apparatus

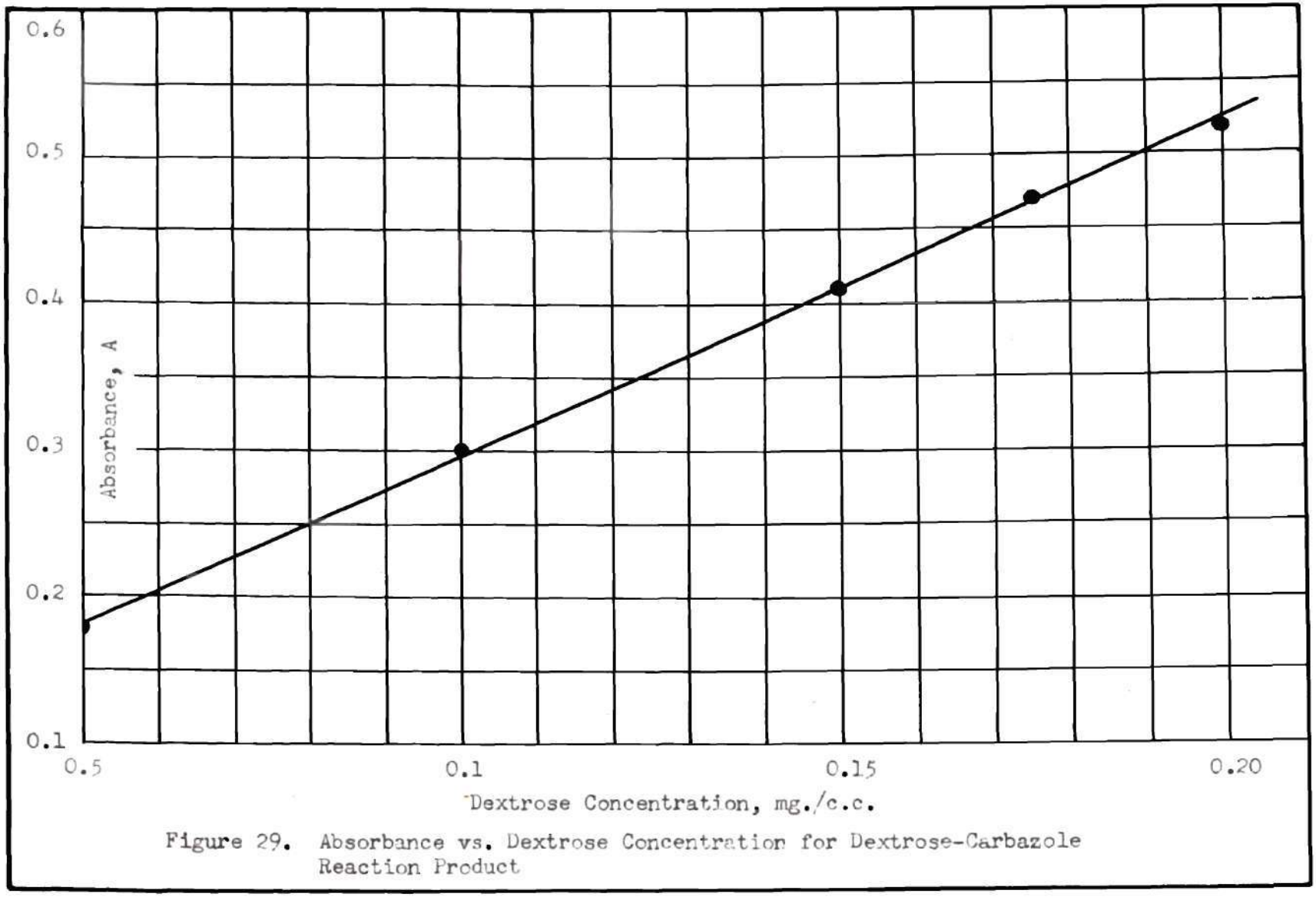


Figure 29. Absorbance vs. Dextrose Concentration for Dextrose-Carbazole Reaction Product

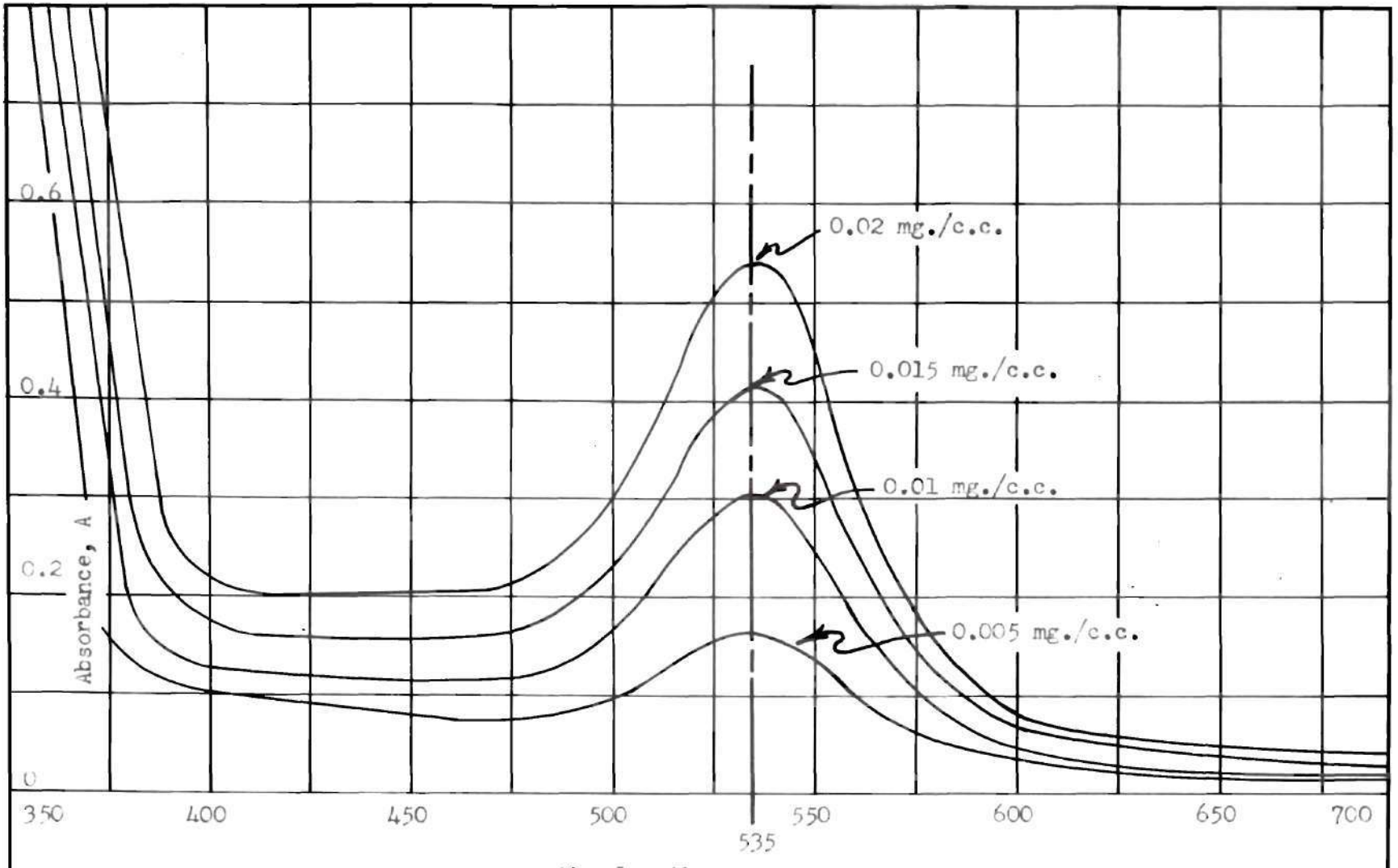


Figure 30, Absorbance vs. Wavelength for Dextrose-Carbazole Reaction Product

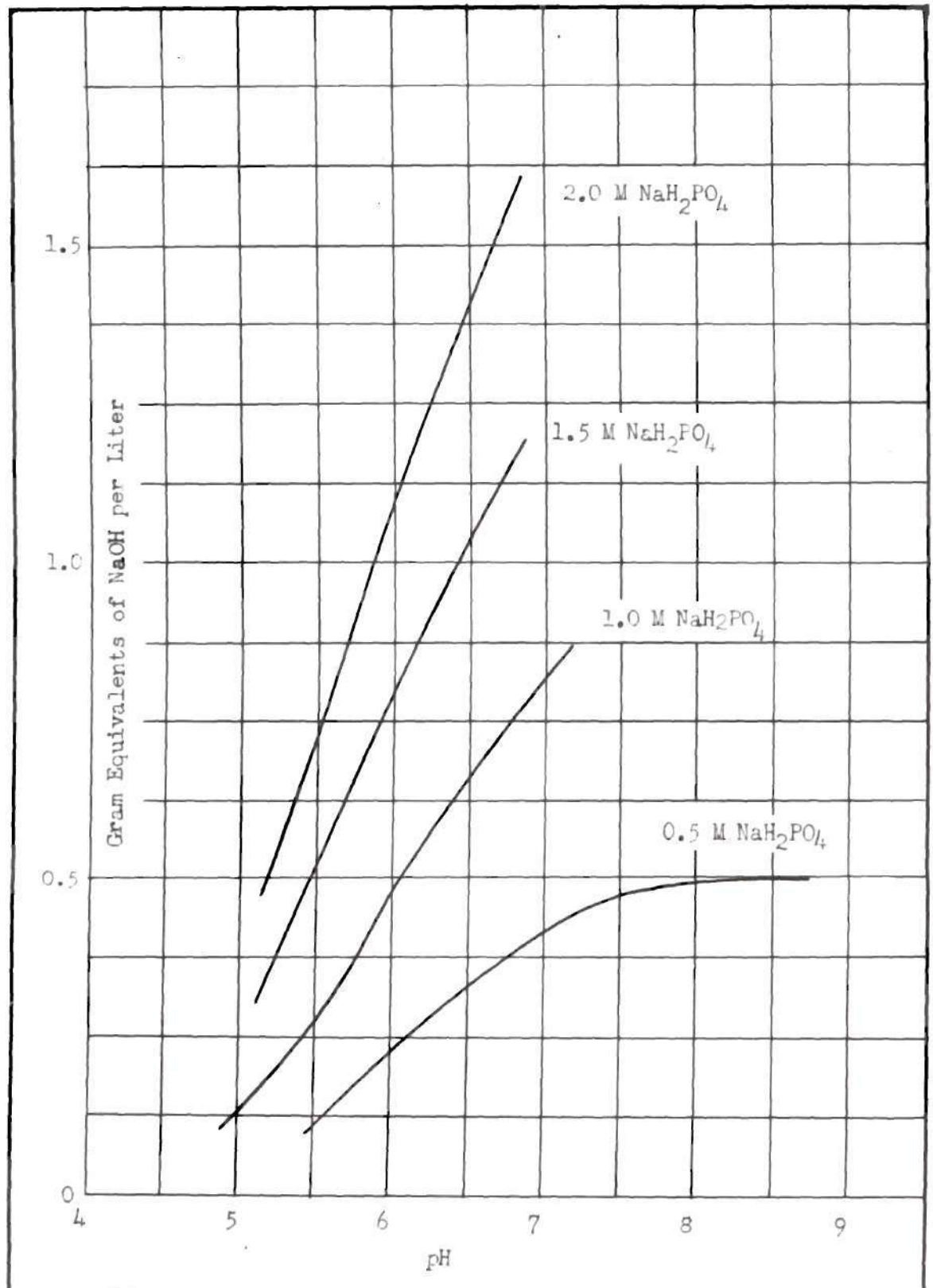


Figure 31. Buffer Characteristics of NaH_2PO_4-NaOH Solutions (Containing 325 g./l. of Dextrose)

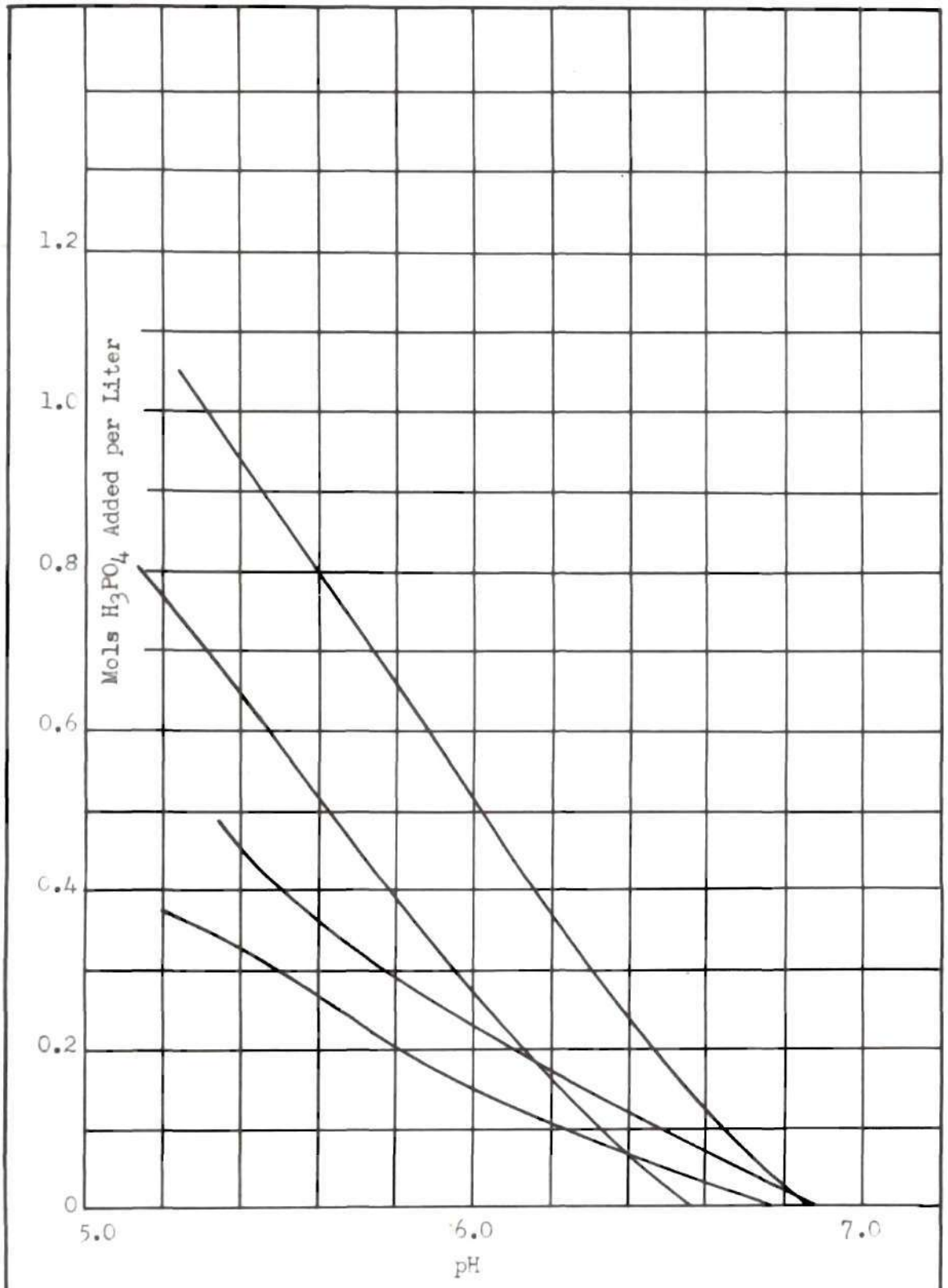


Figure 32. Effect of Addition of Phosphoric Acid on the pH of NaH_2PO_4-NaOH Solutions (Containing 325 g./l. Dextrose)

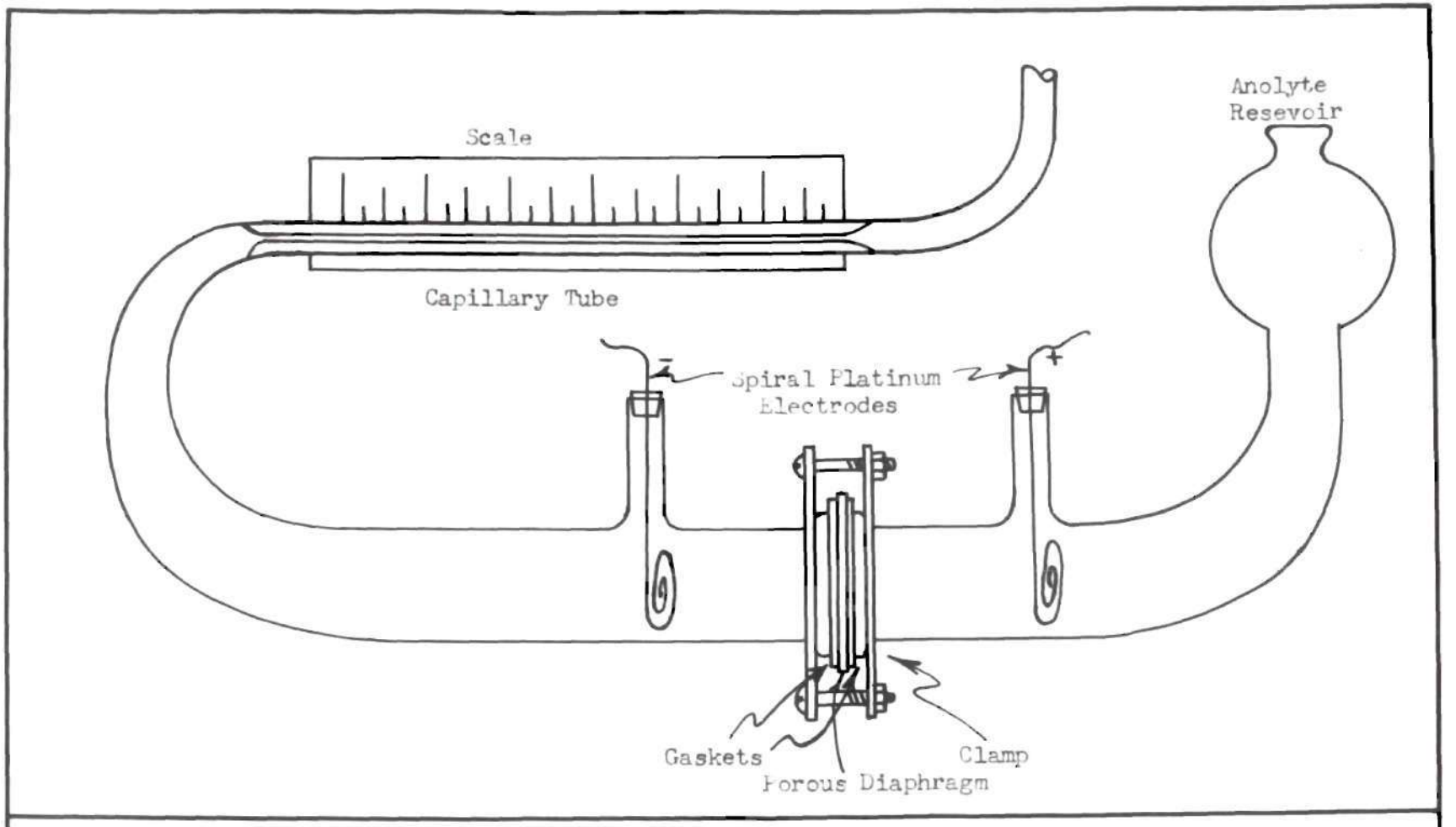


Figure 33. Electroendosmosis Cell Used by R. Bruns (Data of Tables 47, 48, 49 and 50)

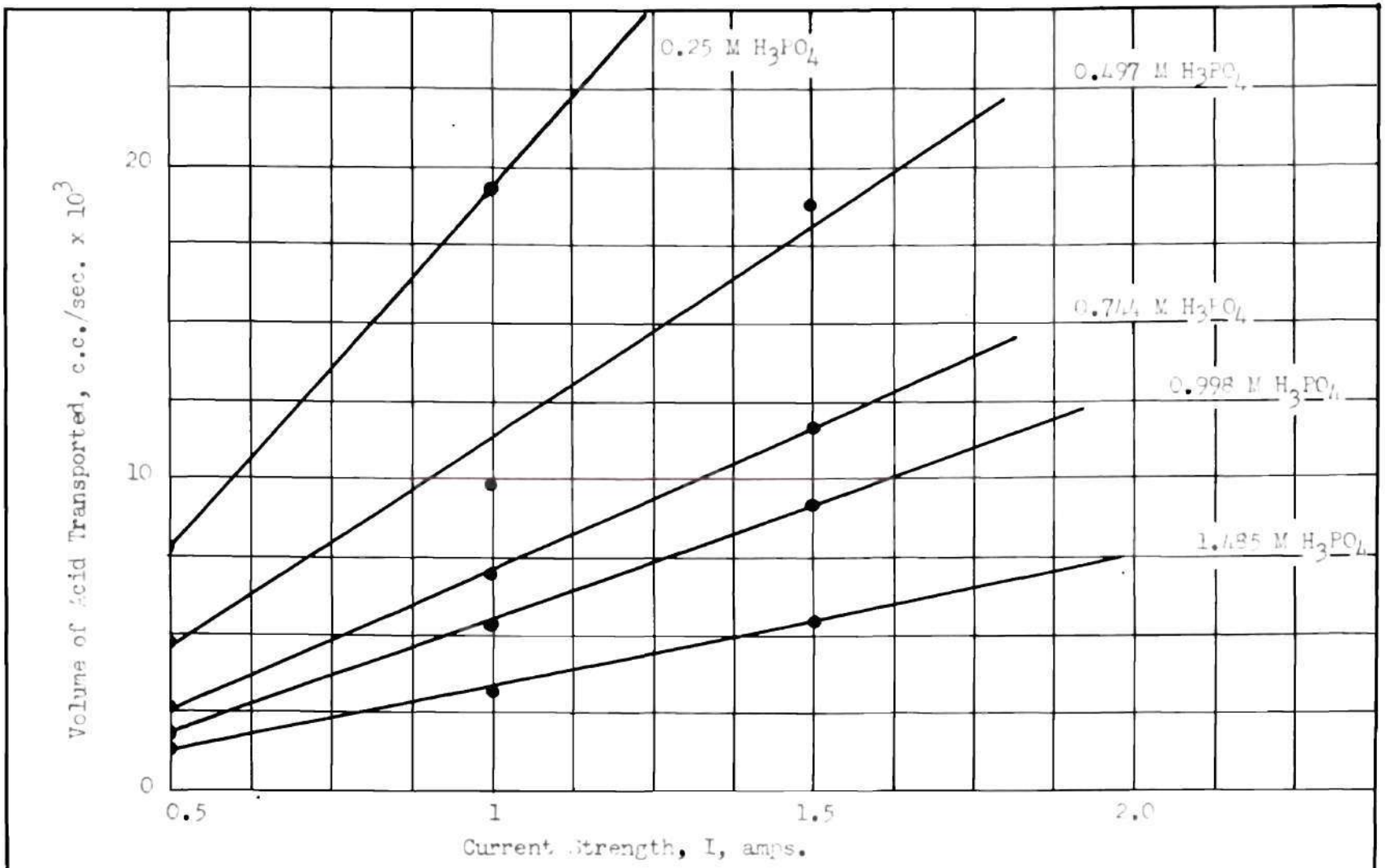


Figure 34. Volume Phosphoric Acid Transported by Electroendosmosis vs. Current Strength

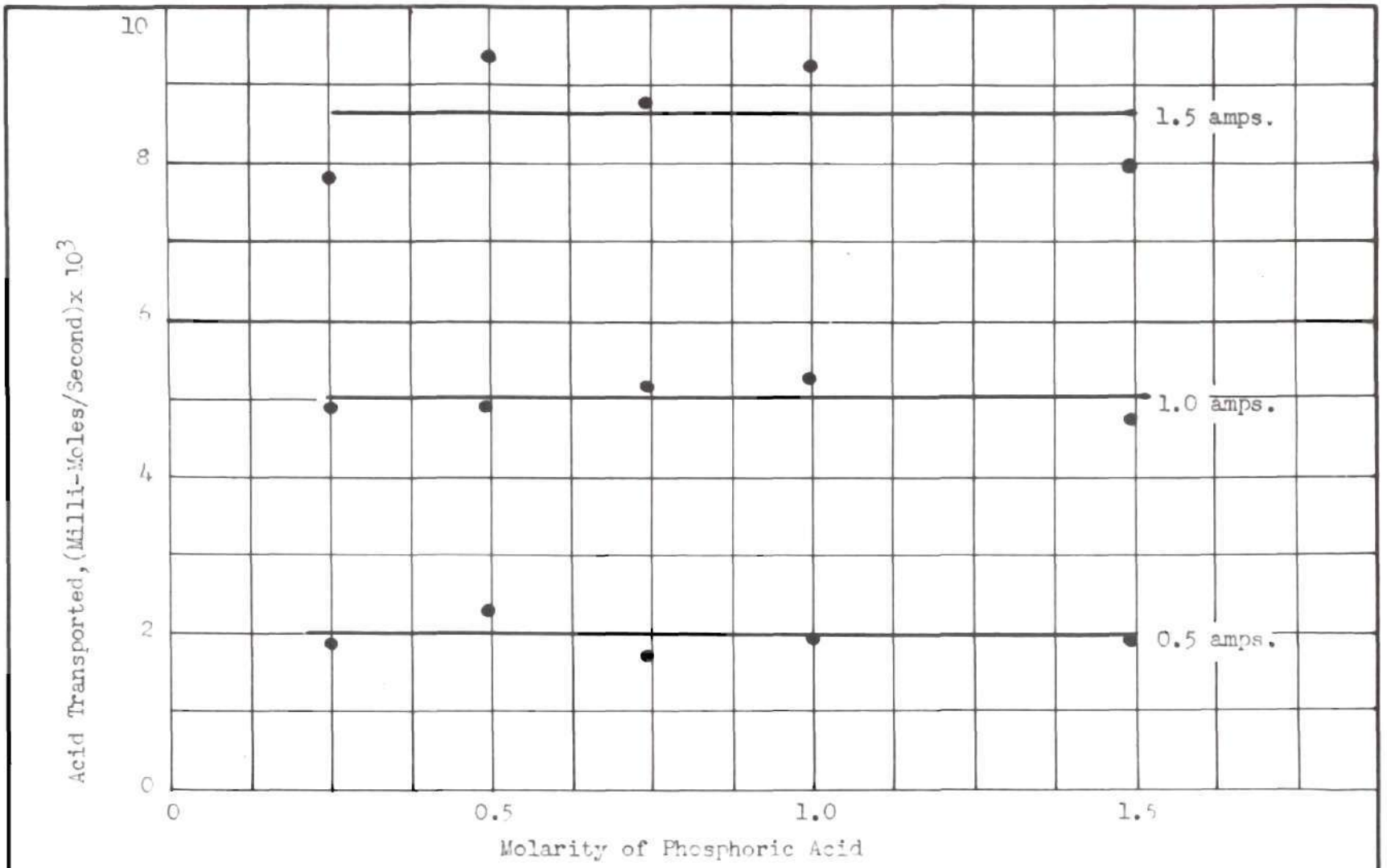


Figure 35. Volume of Phosphoric Acid Transported by Electroendosmosis vs. Acid Molarity

APPENDIX II

Table 46. Data Reported by Emerson in United States Patent 2,561,656

Run No.	Dextrose Conc.	Catholyte Make-up	Anolyte Make-up	Cathode	C.D.	T°C.	Operating Hours	Catholyte pH	S.R. (%)	C.E. (%)	Catholyte Appearance
1	320	1M NaH_2PO_4 3/4M NaOH	2-3M H_3PO_4	Pb	0.70	40-45	22½	4-5	76	43	water white
2	320	"	"	Pb-Hg	0.70	40-45	42	5-6	99	52	"
3	320	"	"	Pb-Hg	0.70	40-45	42	5-6	99	55	"
4	325	"	"	Zn-Hg	0.50	40	24	4-5-6	92	66	"
5	325	"	"	Ni-Hg	0.65	40	24	4-5-6-7	95	50	"
6	325	1M $NaHCO_3$	1M $NaHCO_3$	Ni-Hg	0.5	50	3	6-7	30	very high	light yellow
7	320	1M NaH_2PO_4 3/4M NaOH	2-3M H_3PO_4	Galv-Iron-Hg	1.0	40-45	22½	5-6	76	43	water white

Dextrose conc. is the concentration of anhydrous dextrose in grams per liter.

Catholyte make-up is the initial concentration of electrolyte in the catholyte expressed in moles per liter.

Anolyte make-up is the concentration of anolyte electrolyte in moles per liter.

Cathode is the metal used as cathode.

C.D. is the current density expressed in amps./dm^2.

T°C. is the catholyte operating temperature.

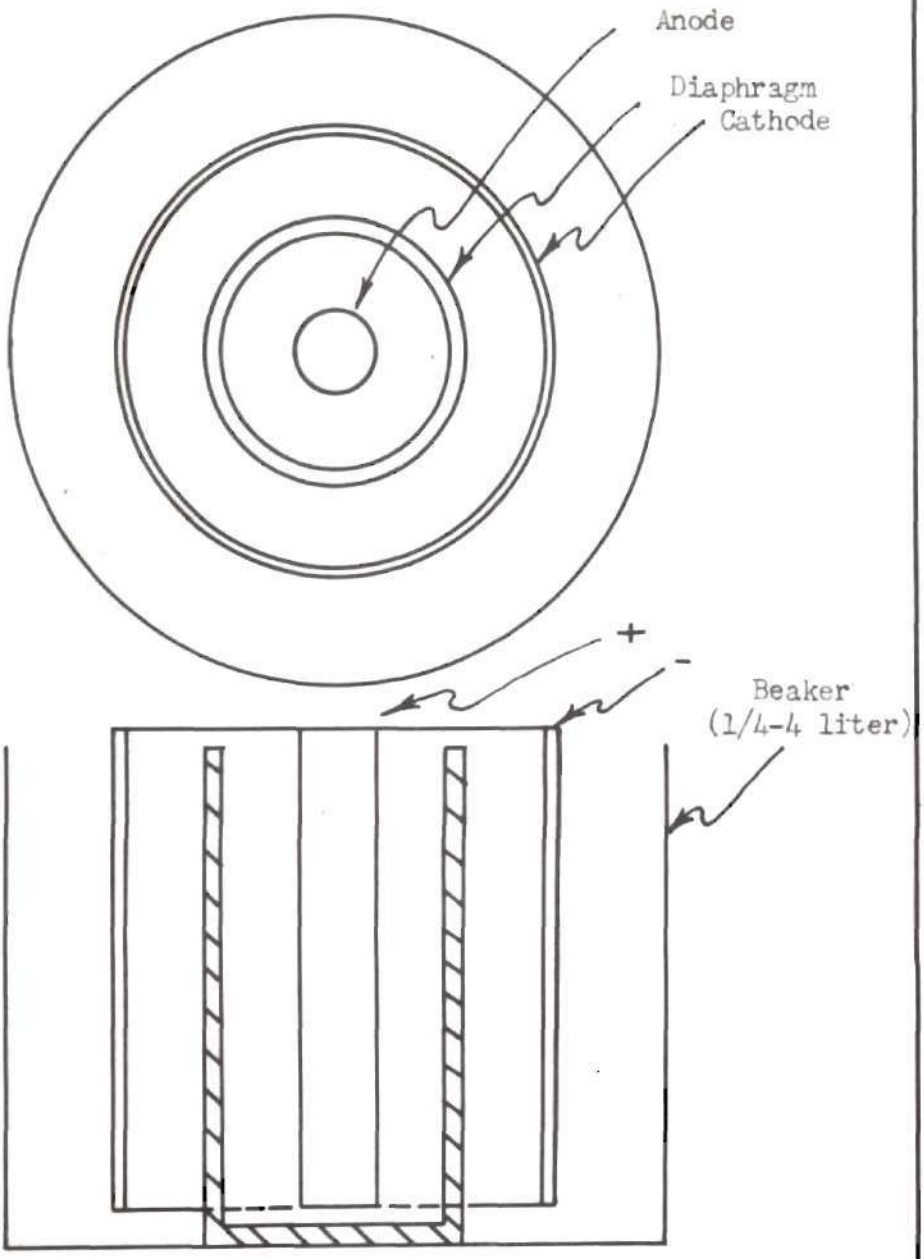
Operating hours indicates the hours of cell operation required to reach the degree of reaction indicated under Per Cent S.R.

Catholyte pH is the pH of the bulk catholyte during the run.

S.R. is the per cent of the original dextrose which has disappeared as determined by Lane and Eynon test.

C.E. is the current efficiency based on dextrose disappearance as measured by the Lane and Eynon test.

Table 46 (Cont'd)



Sketch of type of electrolytic cell used by Emerson to obtain data reported in United States Patent 2,561,656 (Private Communication)

Table 47. Original Data. Flow of Liquid and Flow of Electricity

Initial Catholyte: 300 gms. Dextrose per liter
0.966 M Na_2PO_4
Initial Anolyte: Aqueous H_3PO_4 of various concentrations
Operating Temp.: 46°C.

Run No.	Original Molarity of H_3PO_4 Anolyte	I, Current (amps.)	Duration of Run (min.)	Anolyte Input (gms.)	Anolyte Recovered (gms.)	Loss in Anolyte (gms.)	Cath. Input (gms.)	Catholyte Recovered (gms.)	Cath. Gain (gms.)	Net Loss (gms.)	Liquor flow (Calc. from Catholyte Gain) $(\frac{gms.}{sec.})\times10^{-3}$
1	0.250	0.5	64	100.51	70.13	30.38	29.30	58.34	29.04	1.34	7.56
2	0.250	1.0	32	100.40	61.39	30.01	29.25	66.61	37.36	1.65	19.4
3	0.250	1.5	16	100.32	69.18	31.14	29.27	59.31	30.04	1.10	31.3
4	0.497	0.5	64	101.65	81.63	20.02	29.41	47.67	18.26	1.76	4.75
5	0.497	1.0	32	100.80	79.84	20.96	29.44	48.63	19.19	1.77	10.0
6	0.497	1.5	17	101.93	80.73	21.20	29.40	49.03	19.63	1.57	19.2
7	0.744	0.5	64	102.99	92.60	10.39	29.44	38.39	8.95	1.44	2.33
8	0.744	1.0	32	102.95	87.62	15.33	29.27	42.91	13.64	1.69	7.10
9	0.744	1.5	23	102.95	84.71	18.24	29.40	45.93	16.53	1.71	12.0
10	0.998	0.5	64	204.30	94.77	9.53	29.41	37.27	7.86	1.67	2.05
11	0.988	1.0	32	104.27	92.26	12.01	29.49	40.02	10.53	1.48	5.49
12	0.998	1.5	16	104.32	95.51	10.81	29.42	38.65	9.23	1.58	9.60
13	1.485	0.5	64	106.72	100.78	5.94	29.50	34.52	5.02	0.92	1.31
14	1.485	1.0	32	106.82	100.13	6.69	29.50	35.95	6.45	0.24	3.36
15	1.485	1.5	23	106.75	96.87	9.88	29.36	37.25	7.89	1.99	5.70

Table 48. Summarized Data. Flow of Liquid and Flow of Electricity

Run No.	Original Molarity of H_3PO_4 Anolyte	I, Current (amps.)	1000 V* (cc./sec.)	1000 V/I	Zeta** Potential (volts)
1	0.250	0.5	7.55	15.10	0.11
2	0.250	1.0	19.4	19.4	0.14
3	0.250	1.5	31.2	20.8	0.15
4	0.497	0.5	4.68	9.36	0.12
5	0.497	1.0	9.85	9.85	0.13
6	0.497	1.5	18.9	12.6	0.16
7	0.744	0.5	2.27	4.54	0.09
8	0.744	1.0	6.91	6.91	0.13
9	0.744	1.5	11.7	7.80	0.15
10	0.998	0.5	1.97	3.94	0.10
11	0.998	1.0	5.28	5.28	0.13
12	0.998	1.5	9.24	6.15	0.16
13	1.485	0.5	1.23	2.46	0.10
14	1.485	1.0	3.16	3.16	0.13
15	1.485	1.5	5.35	3.56	0.14

*V = flow rate of liquid thru diaphragm.

**Calculated from equation $Z = 4\pi(300)^2 nKV/DI$. See Glasstone "Textbook of Physical Chemistry", 2nd ed., p. 1223, eq. 41. See p. 1239 (footnote), and p. 6.

Table 49. Analyses of Anolyte and Catholyte

Run No.	Catholyte at end of run			Anolyte at end of run	
	Wt. of 10 ml. Sample (gms.)	5 ml. Sample: ml. base required for first H^-	5 ml. Sample ml. base required for second H^-	Wt. of 10 ml. Sample (gms.)	10 ml. Sample: ml. of base required for first H^-
1	11.7993	3.10	24.34	11.0876	28.20
2	10.7125	3.94	23.67	11.1172	27.60
3	10.7990	3.63	25.31	11.0984	26.47
4	11.1288	3.20	30.70	10.3568	50.40
5	11.1439	3.95	31.40	10.3584	50.62
6	11.1508	3.90	30.23	10.3604	50.06
7	11.4160	2.90	36.20	10.3648	73.10
8	11.2365	2.58	34.85	10.3567	73.52
9	11.1781	4.25	37.46	10.3834	80.16
10	11.4319	3.14	38.40	10.4783	95.42
11	11.3096	3.39	36.78	10.6536	101.66
12	11.3958	3.09	37.09	10.5963	98.64

Table 50. Summarized Data on Flow of Acid

Run No.	Original Molarity of H_3PO_4 Anolyte	I, Current (amps.)	Acid Input in Anolyte (millimols)	Acid Recovery-(millimols)				Acid Loss, % of Input	Observed Loss of Acid from Anolyte (millimols)
				Anolyte	Catholyte	Total	Loss		
1	0.250	0.5	24.9	21.3	3.6	24.9	0	0	3.6
2	0.250	1.0	24.9	18.2	5.3	23.5	1.4	6	6.7
3	0.250	1.5	24.9	19.7	4.3	24.0	0.9	4	5.2
4	0.497	0.5	49.5	43.1	3.0	46.1	3.4	7	6.4
5	0.497	1.0	49.5	42.3	3.7	46.0	3.5	7	7.2
6	0.497	1.5	49.5	42.3	3.7	46.0	3.5	7	7.2
7	0.744	0.5	74.1	70.8	2.1	72.9	1.2	2	3.3
8	0.744	1.0	74.1	67.4	2.1	69.5	4.6	6	6.7
9	0.744	1.5	74.1	70.9	3.8	74.7	-0.6	-0.8	3.2
10	0.998	0.5	99.4	93.5	2.2	95.7	3.7	4	5.9
11	0.998	1.0	99.4	95.4	2.6	98.0	1.4	1	4.0
12	0.998	1.5	99.4	94.4	2.3	96.7	2.7	3	5.0

APPENDIX III

Sample Calculation: Current Efficiency for Run No. 5 Reported in Table 46 (APPENDIX II)

Initial dextrose concentration = 325 g./l.

Data: 95% sugar reduction after 24 hours of operating time

Current density = 0.65 amps./dm^2.

Ratio of cathode area to catholyte volume = 15.4 dm^2./liter.

Basis: 1 liter of catholyte.

The equivalents of electricity passed in 24 hours will be

$$(24 \text{ hours})\left(\frac{3600 \text{ sec.}}{\text{hour}}\right)\left(\frac{0.65 \text{ amps.}}{dm^2}\right)\left(\frac{15.4 dm^2}{\text{liter}}\right)\left(\frac{1 \text{ coulomb}}{\text{amp. sec.}}\right)\left(\frac{\text{equivalent}}{96{,}500 \text{coulombs}}\right)$$

$$= 8.97 \text{ equivalents passed in 24 hours.}$$

In 24 hours 95% of the initial sugar is reduced or (.95)(325) = 309 grams are reacted.

Since 1 mole of dextrose requires 2 equivalents of hydrogen for reduction, the equivalent weight of dextrose is one-half its molecular weight so that the equivalent weight of dextrose is 180.02/2 or approximately 90, and the equivalents of dextrose reduced is then

$$\frac{309 \text{ g.}}{90 \text{ g./equivalent}} = 3.44 \text{ equivalents}$$

and the current efficiency is

$$\frac{3.44}{8.97} \times 100 = 38.3\%$$

The value reported in the patent for this run is 50%.

Similar treatment of the other runs reported evolved the results presented in Table 2. As mentioned in the discussion section, current efficiencies calculated in this manner do not give a true picture of the cell operation.

Sample Calculation: Reaction Rate and Cathode Potential for Run No. 22

Reference to the experimental data for Run No. 22 and the graphical presentation of these results (not shown) indicates that the dextrose concentration decreases at a substantially constant rate in the time interval between 3.5 and 8.08 hours. The cathode potential during this interval changed only slightly.

The disappearance of dextrose from the catholyte during this interval was 13.3 grams, exclusive of that removed as samples. The dextrose disappearance due to diffusion into the anolyte must be subtracted from this figure to obtain the dextrose actually reduced. During the 8.08 hour run, 7.22 grams of dextrose diffused into the anolyte. Assuming a constant rate of diffusion, the hourly loss to the anolyte is $\frac{7.22}{8.08}$ gm./hr. The dextrose reacted per hour is then

$$\frac{(13.3) - \frac{7.22}{8.08}(8.08 - 3.5)}{8.08 - 3.5} = \frac{2.016}{\text{hour}} \text{ grams}$$

The cathode potential during the time interval under consideration is taken as the arithmetic average during the period.

At 3.5 hours the potential measured against the saturated calomel electrode was 1.605 volts. At 8.08 hours, the measured value was 1.620 volts. The arithmetic average of these two values is about 1.612. From the relation

$$P = e_s - E = 0.2415 - E$$

The cathode potential is calculated to be -1.3705 volts.